JUN 20 1933

U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 10 MARCH, 1933 No. 3

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
531.	Temperature coefficient of the moduli of metals and alloys used as elastic elements. G. H. Keulegan and M. R. Houseman	289
532.	A magnetic balance for the inspection of austenitic steel. Raymond L. Sanford	321
533.	Determination of aluminum in nitriding steels by the use of 8-hydroxyquinoline. H. A. Bright and Robert M. Fowler	327
534.	The oxidation of alpha and beta glucose and a study of the isomeric forms of the sugar in solution. Horace S. Isbell and Ward Pigman	337
535.	Scattering of electrons by ions and the mobility of electrons in a cæsium discharge. C. Boeckner and F. L. Mohler	357
536.	The preparation of optically stable sugar solutions for colorimetric analysis. J. F. Brewster and F. P. Phelps	365
537.	Thermoelectric properties of platinum-rhodium alloys. Frank R. Caldwell	373
538.	The vapor pressure of liquid and solid carbon dioxide. C. H. Meyers and M. S. Van Dusen	381
539.	Methods for determining the total acidity of soils. I. A. Denison	413

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

September, 1932 (Vol. 9, No. 3)

RP471. A new determination of the atomic weight of osmium. Raleigh Gilchrist. Price 5 cents.
RP472. "Moisture expansion" of ceramic whiteware. R. F. Geller and A. S. Creamer. Price 5 cents.
RP473. Infra-red arc spectra photographed with xenocyanine. W. F. Meggers and C. C. Kiess. Price 5 cents.
RP474. Tensile properties of cast nickel-chromium-iron alloys and of some alloy steels at elevated temperatures. William Kahlbaum and Louis Jordan. Price 5 cents.
RP475. The comparison of high voltage X-ray generators. Lauriston S. Taylor and K. L. Tucker. Price 5 cents.
RP476. The structure of the chromic-acid plating bath: The theory of chromium deposition. Charles Kasper. Price 5 cents.
RP477. Physical properties and weathering characteristics of slate. D. W. Kessler and W. H. Sligh. Price 5 cents.
RP478. Radiation from cæsium and other metals bombarded by slow electrons. C. Boeckner. Price 5 cents.
RP479. A simplified precision formula for the inductance of a helix with corrections for the lead-in wires. Chester Snow. Price 5 cents.
RP480. Register studies in offset lithography. C. G. Weber and R. M. Cobb. Price 5 cents.
RP481. Creep at elevated temperatures in chromium-vanadium steels containing tungsten or molybdenum. William Kahlbaum and Louis Jordan. Price 5 cents.

October, 1932 (Vol. 9, No. 4)

RP482. The synthesis, purification, and certain physical constants of the normal hydrocarbons from pentane to dodecane, of *n*-amyl bromide and of *n*-nonyl bromide. B. J. Mair. Price 5 cents.
RP483. A study of some ceramic bodies of low absorption maturing at temperatures below 1,000° C. R. F. Geller and D. N. Evans. Price 5 cents.
RP484. The determination of magnesia in phosphate rock. James I. Hoffman. Price 5 cents.
RP485. Collisions of the first and second kind in the positive column of cæsium discharge. F. L. Mohler. Price 5 cents.
RP486. The areas and tensile properties of deformed concrete-reinforcement bars. A. H. Stang, L. R. Sweetman, and C. Gough. Price 5 cents.
RP487. A calorimetric method for determining the intrinsic energy of a gas as a function of the pressure. Edward W. Washburn. Price 5 cents.
RP488. The photographic emulsion: Variables in sensitization by dyes. Burt H. Carroll and Donald Hubbard. Price 5 cents.
RP489. A method for the separation of rhodium from iridium and the gravimetric determination of these metals. Raleigh Gilchrist. Price 5 cents.
RP490. The isoelectric point of silk. Milton Harris. Price 5 cents.
RP491. Effective applied voltage as an indicator of the radiation emitted by an X-ray tube. Lauriston S. Taylor, George Singer, and C. F. Stoneburner. Price 5 cents.
RP492. Column curves and stress-strain diagrams. William R. Osgood. Price 5 cents.

November, 1932 (Vol. 9, No. 5)

RP493. The variation with angle of emission of the radiation from metals bombarded by slow electrons. C. Boeckner. Price 5 cents.
RP494. Nitrogen content of some standard sample steels. J. G. Thompson and E. H. Hamilton. Price 5 cents.
RP495. Analytical methods for the determination of levulose in crude products. R. F. Jackson, J. A. Mathews, and W. D. Chase. Price 5 cents.
RP496. Determination of alumina and silica in steel by the hydrochloric acid residue method. J. G. Thompson and J. S. Acken. Price 5 cents.
RP497. An analysis of lanthanum spectra La I, La II, La III. Henry Norris Russell and William F. Meggers. Price 10 cents.
RP498. Analysis of weighted silk. Ralph T. Mease. Price 5 cents.
RP499. The heat of formation of hydrogen chloride and some related thermo-dynamic data. Frederick D. Rossini. Price 5 cents.
RP500. Thermal expansion of lead. Peter Hidnert and W. T. Sweeney. Price 5 cents.

Research papers, where price is given, are already available, and others will be available in the near future as separates for purchase from the Superintendent of Documents, United States Government Printing Office, Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
ROY D. CHAPIN, Secretary
BUREAU OF STANDARDS
LYMAN J. BRIGGS, Acting Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

March, 1933
Vol. 10, No. 3

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON: 1933

For sale by the Superintendent of Documents, Washington, D. C. - - Price 25 cents; $2.50 per year on subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH see pages 2 and 3 of the cover

TEMPERATURE COEFFICIENT OF THE MODULI OF METALS AND ALLOYS USED AS ELASTIC ELEMENTS

By G. H. Keulegan and M. R. Houseman

ABSTRACT

In continuation of the work reported in N. A. C. A. Technical Report No. 358, the temperature coefficients of the modulus of rigidity and of Young's modulus of elasticity of 31 alloys and metals have been determined in the temperature range $-50°$ to $+50°$ C. These were selected on the basis of their possible use as elastic elements for aircraft and other instruments. In most cases the temperature coefficients were determined with the metal in the condition of heat treatment or cold work most suitable for its use as an elastic element and also in the annealed condition. The coefficient of each modulus at 0° C., the ratio of the coefficient at $+25°$ to that at $-25°$ C., the composition and the heat treatment or cold work are given for each sample. The temperature coefficient of Poisson's ratio and the significance of the differences in the two coefficients for a given material are discussed.

CONTENTS

	Page
I. Introduction	290
II. Temperature coefficient of the modulus of rigidity	290
1. Theory	290
(*a*) Derivation of the working formula	290
(*b*) The effect of elastic afterworking and permanent set in the springs	293
2. Description of apparatus	294
(*a*) Apparatus principally used	294
(*b*) Apparatus for testing small springs	295
3. Materials	297
(*a*) Chemical composition	297
(*b*) Form and dimensions of springs	297
(*c*) Heat treatment and hardness	298
4. Experimental procedure and results	299
(*a*) Experimental procedure	299
(*b*) Corrections applied to the readings	300
(*c*) Method of reducing the data	301
(*d*) Extension at zero tension	303
(*e*) Experimental results	304
(*f*) Accuracy of results	304
III. Temperature coefficient of Young's modulus of elasticity	307
1. Derivation of the working formula	307
2. Description of the apparatus	309
3. Materials	310
4. Experimental procedure and results	310
(*a*) Experimental procedure	310
(*b*) Method of reducing the data	310
(*c*) Effect of temperature at initial zero angular deflection	312
(*d*) Experimental results	314
(*e*) Accuracy of results	314
IV. Discussion	315
1. Anomalous behavior of stainless steel	315
2. Relative values of the temperature coefficients	317
3. Variation of the temperature coefficients of the moduli with temperature	317
4. Temperature coefficient of Poisson's ratio	318
5. Effect of heat treatment on the temperature coefficients of the elastic moduli	319
V. Conclusions	320
VI. Acknowledgments	320

I. INTRODUCTION

This investigation is an extension of that made by Brombacher and Melton,[1] and was made with the financial support and cooperation of the National Advisory Committee for Aeronautics.

In order that the performance of aircraft instruments be considered satisfactory their indications should be independent of temperature in approximately the range $-50°$ to $+50°$ C. The effect of temperature on instruments of correct mechanical design is due largely to the change in the elastic moduli with temperature of the elastic elements used. Among these elements are the diaphragm capsules and springs of pressure-measuring instruments, the springs of accelerometers and tachometers, and the hair springs of electrical instruments. Data on the temperature coefficients of the elastic moduli are of primary value.

This investigation was undertaken: (*a*) To measure, in the temperature range $-50°$ to $+50°$ C., the temperature coefficients of both the modulus of rigidity and Young's modulus of elasticity of various metals and alloys of possible use for diaphragms and springs, including materials having small (or anomalous) temperature coefficients. (*b*) To determine the effect on the temperature coefficients of annealing, cold working, or tempering the materials.

Brombacher and Melton used a torsion pendulum to determine the temperature coefficient of the modulus of rigidity and the effect of stress and heat treatment on both the modulus and the temperature coefficient. This method has serious disadvantages. In selecting a more suitable experimental method consideration was given to the practical necessity of obtaining temperature control by means of a liquid bath and to the desirable possibility of obtaining the data on both moduli from the same specimen of a given material. This led to the use of helical spring specimens. Two springs of the given material and of the same design were coupled together and (*a*) stressed in tension to obtain the temperature coefficient of the rigidity modulus and (*b*) stressed in twist to obtain the temperature coefficient of Young's modulus of elasticity. While under each type of stress the change in the deformation of the springs of the coupled system was measured as the temperature of one of the springs was varied while that of the other spring was maintained constant. The use of two springs was necessary to eliminate lateral vibration and to a large extent the effect of elastic afterworking or drift. If the two springs were exactly alike the drift would not change the deflection of the springs since their actions opposed each other.

II. TEMPERATURE COEFFICIENT OF THE MODULUS OF RIGIDITY

1. THEORY

(a) DERIVATION OF THE WORKING FORMULA

Consider an ideal arrangement of the parts of the apparatus used to determine the temperature coefficient of rigidity as shown diagrammatically in Figure 1. Two helical springs s_1 and s_2, similar in construction and material, are attached to a base BB by means of the

[1] W. G. Brombacher and E. R. Melton, N. A. C. A. Technical Report No. 358, 1930.

links a_1 and a_2. Spring s_2 is the test spring and spring s_1 the auxiliary spring. During a test the temperature of the test spring is varied while that of the auxiliary spring is kept constant. The upper ends of these springs are connected to the ends of a horizontal lever P_1, P_2 by means of the connecting links b_1 and b_2. The center of the lever rests on a support E which is adjustable in length. Each spring is immersed in a liquid temperature bath.

When both springs are at the temperature θ_1 we denote their stiffnesses by S_1 and S_2. When the length of E is so adjusted that the springs are not stressed the heights of P_1 and P_2 above a fixed reference plane are X_{10} and X_{20}. With both springs at the same temperature θ_1 the auxiliary and test springs are deflected by increasing the length of E until the heights of P_1 and P_2 above the reference plane are X_1 and X_2. Since the spring reactions are equal in magnitude, we have

$$(X_1 - X_{10})S_1 = (X_2 - X_{20})S_2 \tag{1}$$

If now the temperature of the bath surrounding the test spring is increased by a small amount, the temperature of the bath surrounding

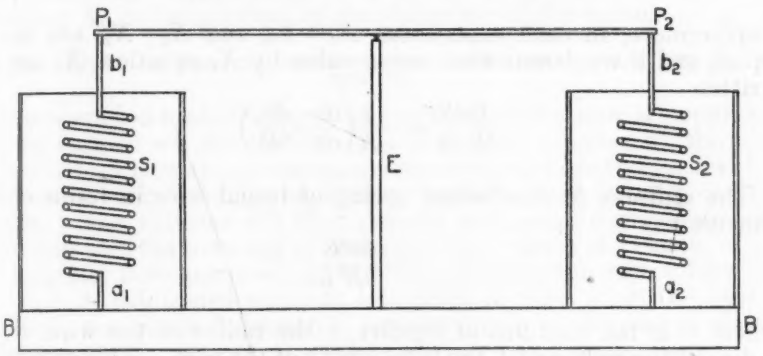


FIGURE 1.—*Simplified diagram of the apparatus for the determination of the temperature coefficient of the rigidity modulus*

the auxiliary spring being kept constant, the deflections X_1 and X_2 are altered, the stiffness S_2 is modified and, because of the thermal expansion of the spring and the connecting links a_2 and b_2, the position of zero stress in the springs will also be changed. The rate of change may be determined by differentiating equation (1) with respect to temperature. We thus obtain

$$S_2\left(\frac{dX_2}{d\theta} - \frac{dX_{20}}{d\theta}\right) + (X_2 - X_{20})\frac{dS_2}{d\theta} = S_1\left(\frac{dX_1}{d\theta} - \frac{dX_{10}}{d\theta}\right)$$

Since the springs are coupled together in opposition

$$\frac{dX_1}{d\theta} = -\frac{dX_2}{d\theta} \text{ and } \frac{dX_{10}}{d\theta} = -\frac{dX_{20}}{d\theta}$$

whence

$$(S_1 + S_2)\left(\frac{dX_2}{d\theta} - \frac{dX_{20}}{d\theta}\right) = -(X_2 - X_{20})\frac{dS_2}{d\theta} \tag{2}$$

But from equation (1)

$$S_1 = \frac{S_2(X_2 - X_{20})}{X_1 - X_{10}}$$

Introducing this expression into equation (2) we find

$$\frac{1}{S_2}\frac{dS_2}{d\theta} = -\left(\frac{1}{X_1 - X_{10}} + \frac{1}{X_2 - X_{20}}\right)\left(\frac{dX_2}{d\theta} - \frac{dX_{20}}{d\theta}\right) \tag{3}$$

It is clear, since S_1 does not appear in this equation, that it is not necessary that the temperatures of the two springs be initially the same, but it is essential that the auxiliary spring be kept at a constant temperature. In the experiments to be described, the change in X_2 was measured, starting from the condition when the temperature of the test springs was $+50°$ C. Changes in X_2 and X_{20} thus measured are denoted by x and x_0, respectively. It is obvious that

$$\frac{dX_2}{d\theta} = \frac{dx}{d\theta} \text{ and } \frac{dX_{20}}{d\theta} = \frac{dx_0}{d\theta}$$

Furthermore, in each experiment $X_1 - X_{10}$ and $X_2 - X_{20}$ are nearly equal, and if we denote their mean value by X, equation (3) may be written

$$\frac{1}{S_2}\frac{dS_2}{d\theta} = -\frac{2}{X}\left(\frac{dx}{d\theta} - \frac{dx_0}{d\theta}\right) \tag{4}$$

The stiffness S of a helical spring of round wire in terms of the constants is

$$S = \frac{\pi r^4 G}{2R^2 L} \tag{5}$$

where G is the modulus of rigidity, r the radius of the wire, R the radius of the coils, and L the total length of the wire. This expression can also be written

$$S = KLG \tag{6}$$

where K is a numerical constant of the spring and L has the dimensions of length. K is not affected by temperature if the ratios of r/R and r/L remain unaltered with temperature.

If equation (6) be differentiated with respect to θ and the result be divided by equation (6), we obtain

$$\frac{1}{S}\frac{dS}{d\theta} = \alpha + \frac{1}{G}\frac{dG}{d\theta}$$

α being the thermal coefficient of linear expansion. Introducing this in equation (4) there results

$$\frac{1}{G}\frac{dG}{d\theta} = -\frac{2}{X}\left(\frac{dx}{d\theta} - \frac{dx_0}{d\theta}\right) - \alpha \tag{7}$$

We place

$$\frac{1}{G}\frac{dG}{d\theta} = m \tag{8}$$

Equation (7) is the working formula for the experiments. The term m is by definition the temperature coefficient of the rigidity modulus. The quantity $\frac{dx}{d\theta}$ is the rate of change of the deflection of the test spring with temperature and is a function of the temperature and of the deflection $X_2 - X_{20}$. It is determined graphically from the experimentally determined curves of x as a function of the temperature for different initial deflections.

The quantity $\frac{dx_0}{d\theta}$ is the rate of change of the deflection of the spring with temperature at zero initial deflection; that is, for the spring in the initially unstressed condition. If it were not for the anomalous effects of internal stresses in the spring, $\frac{dx_0}{d\theta}$ could be computed from the thermal expansion of parts of the apparatus and of the spring. In the method actually adopted and known to be more reliable, $\frac{dx}{d\theta}$ is determined for several deflections and the data graphically extrapolated to zero deflection. This extrapolation involves the reasonable assumption that X_{20} is independent of the deflection of the spring.

(b) THE EFFECT OF ELASTIC AFTERWORKING AND PERMANENT SET IN THE SPRINGS

Consideration must also be given to the effect of elastic afterworking and permanent set, since when these two effects are present, the stiffness of the springs at a given temperature is no longer constant as has been assumed in deriving the working formula given in the preceding section. The stiffness will then depend to a small degree upon the deflection and the duration of the deflection. Both the elastic afterworking and permanent set are increases in deflection with time while the load is maintained constant but differ in that, when the load is removed, the excess deflection is recovered only in the case of elastic afterworking.

The effect of permanent set and elastic afterworking were minimized by the experimental method adopted. Only the differential amount of these quantities for the two springs has an effect, as long as the actual amount of the set or elastic afterworking is of the second order compared with the deflections X_1 and X_2. The differential amount was kept small by using springs of the same material and of similar design. However, it was necessary to determine whether or not the effect was excessive in individual cases. For this purpose a theoretical analysis was made which showed that the change in the observed deflection due to elastic afterworking is at its maximum at the completion of the temperature cycle. Therefore, it is only necessary to note the difference between the initial reading and the final reading at the instant of completing the cycle, which if negligible, proves that the elastic afterworking is negligible. It is further evident that this difference also included the differential permanent set and thus this single criterion is sufficient for both if the difference is negligible.

2. DESCRIPTION OF APPARATUS

(a) APPARATUS PRINCIPALLY USED

The apparatus used for the measurement of the temperature coefficient of the rigidity modulus is shown in Figures 2 and 3. The bath for controlling the temperature of the springs s_1 and s_2 is con-

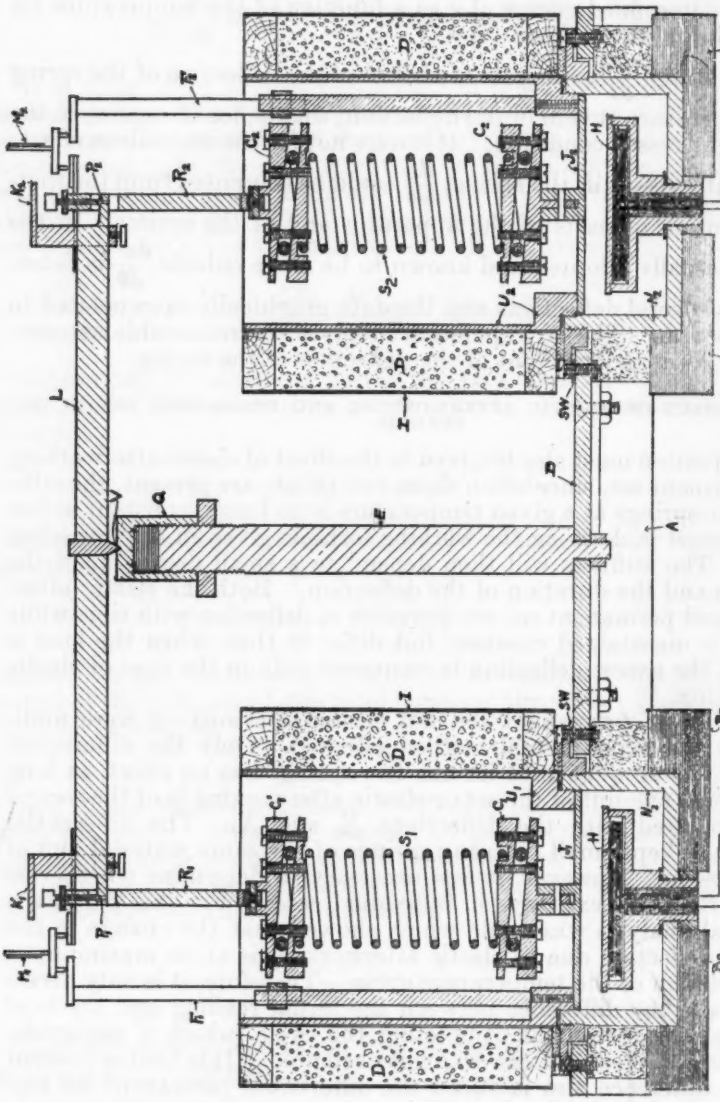


FIGURE 2.—*Cross-sectional diagram of the apparatus for the determination of the temperature coefficient of the rigidity modulus*

See the text for meaning of the letters

tained in the vessels formed by the removable cylinders U_1 and U_2 and the cups N_1 and N_2 which are permanently fastened to the base B. The springs are supported at their lower ends by slotted steel bars J_1 and J_2 which are attached to the heavy rings forming the lower end of U_1 and U_2. Similar clamps C_1 and C_2 are attached to each end of

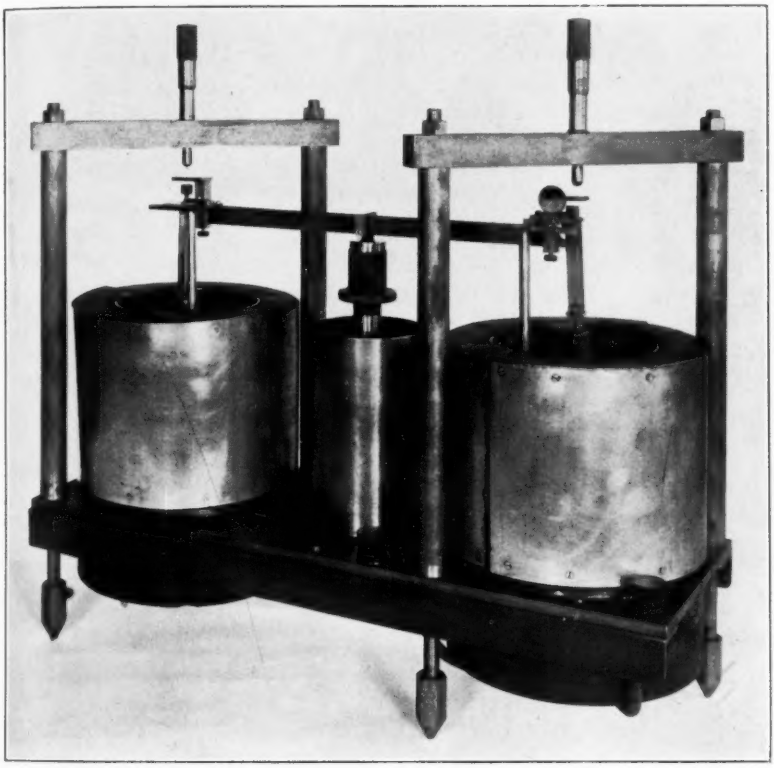


FIGURE 3.—*Apparatus for the determination of the temperature coefficient of the rigidity modulus*

UNIV OF MICH

the springs. The upper end of spring s_1 is connected to the lever L by means of the steel link R_1 and spring s_2 by the invar link R_2. These links are attached to the clamps by universal joints. The adjustable pivots P_1 and P_2 at the upper ends of the links rest in small holes near the extremities of the lever arm L. The arm L rests on a centrally attached knife-edge in a V groove of the screw cap Q of the central rod E. The function of the screw cap is to raise or to lower the lever arm L. Central rod E is permanently attached to the steel base plate B. The latter is 0.25 inch thick and is reinforced on each side by the angle irons A. This additional rigidity was essential.

Two micrometers (not shown in the figure) were used to measure the vertical displacement (X in equation (7)) of the lever arm L at the end platforms K_1 and K_2, located almost vertically above the springs. The rotating mirrors M_1 and M_2 were parts of an optical lever and were used for measuring the change in the end deflections of the lever arm as the temperature of the test spring s_2 was varied. The upper rod F_1 of the support for mirror M_1 was made of steel and rod F_2 of invar. The lower rods of the support were of steel and were attached to the heavy rings of the bath vessels U_1 and U_2.

The electrical heaters H are placed, as shown in Figure 2, in the lower cups N_1 and N_2 of the bath vessels. In order to reduce the transfer of heat to or from the base plate B to a minimum, each cup is attached to the base only at four points by means of the screw and washer assembly SW. The bath is insulated at the bottom by the bakelite cover Ba, and at the sides by felt and the circular boxes I are filled with powdered cork D. Alcohol was used as the bath liquid. To obtain low temperatures solid carbon dioxide was dropped into the alcohol.

(b) APPARATUS FOR TESTING SMALL SPRINGS

Samples of three materials—tungsten, elinvar, and modulvar—were of much smaller diameter than that of the others. Springs of the size otherwise required would not support the frame of the apparatus for measuring the temperature coefficient of Young's modulus of elasticity (to be described later) and the stiffness was believed to be too small in comparison with the friction of the knife-edge in the apparatus for the rigidity modulus and would thereby introduce considerable error into the measurements. For this reason another apparatus was constructed which had the added advantage that it could be used to measure both temperature coefficients.

The general arrangement of the parts is shown in Figure 4. Quartz rods Q were used for the vertical supports. The springs s_1 and s_2 were rigidly clamped together by means of a small quartz rod Q_1 and were given the required extension or twist by raising or turning the rod R. Two springs were necessary in order to hold the test spring vertical and to reduce the lateral vibrations which it seemed impossible to eliminate. The lower or test spring was immersed in a bath of alcohol, the temperature of which was controlled by an electric heater and solid carbon dioxide. The temperature of the upper or auxiliary spring, which was uncontrolled, was determined by means of copper-constantan thermocouples mounted at points C_1 and C_2. The temperature at point C_3 was also determined in order to be able to correct the spring deflection for the change in length of the brass rod R. The change in the extension of the springs, as the temperature of the test

spring was varied, was measured by means of the optical system shown in Figure 4. The mirror M was pivoted, a deflection of the spring causing the mirror to rotate. The connecting wire T was of tungsten which was used because of its small temperature coefficient of expansion. A small counterweight W kept the wire under a

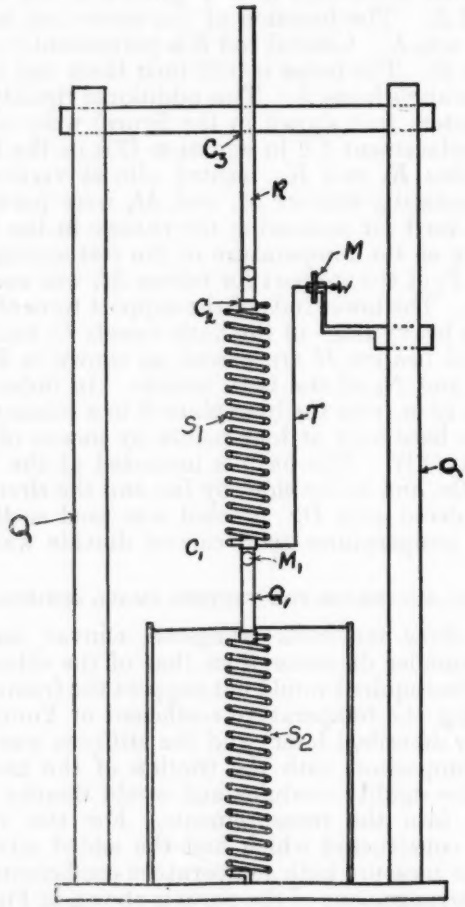


FIGURE 4.—*Simplified diagram of the apparatus used for the determination of the temperature coefficient of the elastic moduli of materials of which only fine wire was available*

constant tension. The method of computing the temperature coefficients is essentially the same as that for springs of larger wires.

In determining the temperature coefficient of Young's modulus, mirrors M_1 mounted on the quartz rod Q_1 were used to measure both the initial angular deflection and the change in angular deflection as the temperature was varied.

3. MATERIALS

(a) CHEMICAL COMPOSITION

The chemical composition of each of the materials is given in Table 1. The analyses were made by the chemistry division.

TABLE 1.—*Chemical composition of the materials*

(a) NONFERROUS

Specimen No.	Material	Elements (in per cent)												
		Cu	Zn	Al	Pb	Sn	Ni	Si	Fe	P	Mn	Mg	C	Be
3	Phosphor bronze	95.3	n. d.	------	n. d.	4.3	n. d.	------	n. d.	0.4	------	------	------	------
14	....do	94.6	n. d.	------	n. d.	5.1	[1] 0.01	------	n. d.	.29	n. d.	------	------	------
15	....do	95.0	n. d.	------	n. d.	4.6	n. d.	------	n. d.	.29	n. d.	------	------	------
10	Monel metal	33.2	------	------	------	------	63.8	0.03	1.7	------	1.1	------	0.10	------
16	Nickel silver	61.7	27.4	------	n. d.	.03	10.5	------	[1] .05	------	[1] .03	------	------	------
17	....do	62.2	23.5	------	n. d.	n. d.	14.2	------	[1] .05	------	[1] .03	------	------	------
18	....do	64.4	16.2	------	n. d.	n. d.	19.3	------	[1] .05	------	[1] .03	------	------	------
19	....do	64.8	25.4	------	n. d.	n. d.	9.8	------	[1] .05	------	[1] .03	------	------	------
20	....do	60.4	24.2	------	n. d.	n. d.	15.3	------	[1] .05	------	[1] .03	------	------	------
21	....do	64.5	17.0	------	n. d.	n. d.	18.4	------	[1] .05	------	[1] .03	------	------	------
27	Duralumin	4.4	------	[2] 93.63	n. d.	------	------	.27	.58	------	.61	0.51	------	------
30	Brass	73.0	[2] 26.93	------	[1] 0.02	------	n. d.	------	[1] .05	------	------	------	------	------
34	Beryllium bronze	98.1	------	------	------	------	------	------	------	------	------	------	------	1.9

(b) FERROUS

Specimen No.	Material	Elements (in per cent)									
		C	Mn	P	S	Cr	Si	V	Ni	W	Fe
1	Chromium vanadium steel	0.53	0.54	0.014	0.025	0.98	0.28	0.24	------	------	------
4	Piano wire	.94	.34	.023	.018	------	------	------	------	------	------
11	....do	.86	.34	.025	.019	------	.19	------	------	------	------
5	Oil-tempered wire	.66	.80	.009	.040	------	------	------	------	------	------
12	....do	.67	.78	.016	.034	------	.13	------	------	------	------
8	Nickel steel	.13	.48	.018	.019	------	------	------	4.97	------	------
9	....do	.18	.48	.010	.016	------	------	------	3.50	------	------
6	High-carbon steel	.83	.64	.030	.024	------	------	------	------	------	------
13	....do	.89	.36	.01	.02	------	.16	------	------	------	------
22	Stainless steel (KA2)	.14	------	------	------	17.4	------	------	8.63	------	------
23	....do	.05	------	------	------	17.5	------	------	8.97	------	------
24	Stainless steel (Enduro A)	.08	------	------	------	17.6	------	------	.13	------	------
25	Stainless steel (Enduro AA)	.06	------	------	------	17.3	------	------	.18	------	------
26	Stainless steel No. 12	.08	------	------	------	11.6	------	------	.65	------	------
29	Silico-manganese steel	.58	1.13	------	------	------	1.88	------	------	------	------
31	Elinvar	.84	1.5	------	------	11.1	.14	------	32.7	3.9	[2] 49.8
32	Modulvar	.16	.18	------	------	.12	.14	------	34.9	n. d.	[2] 64.5

[1] Less than. [2] By difference. n. d.=not detected.

(b) FORM AND DIMENSIONS OF SPRINGS

The materials were obtained in the form of wires about 3 mm (0.125 inch) in diameter with the exception of those of elinvar, modulvar, and tungsten which were about 1.6 mm (0.06 inch) in diameter. The helical springs wound from the larger wires had the following approximate dimensions: Diameter of the coils, 3.7 cm (1.5 inches), length of unstressed spring 9 cm (3.6 inches) and number of coils, 11. The dimensions of those made from the smaller wires were:

Diameter of the coils, 2 cm (0.8 inch); length of unstressed springs, 9 cm (3.6 inches); and number of coils, 16.

(c) HEAT TREATMENT AND HARDNESS

The heat treatment and the Vicker's hardness number of the springs after winding are given in Table 2. The heat treatments were in most cases made by the metallurgical division.

TABLE 2.—*Heat treatment and hardness number of springs*

Spring No.	Specimen No.	Material	Vicker's hardness No.	Heat treatment
1a	1	Chromium vanadium steel	534	N, 900° C., air cooled; OQ, 850° C.; T, 370° C.
1b	1	do	210	N, 900° C., air cooled; A, 850° C.
3a	3	Phosphor bronze	261	Held at 100° C. for one and one-half hours.
4a	4	Piano wire, No. 1	521	Held at 100° C. for one hour.
4b	4	do		N, 800° C. one-half hour, air cooled; A, 790° C. one hour, furnace cooled.
5a	5	Oil tempered wire, No. 1	476	Held at 100° C. for one hour.
5b	5	do		N, 815° C. one-half hour, air cooled; A, 790° C. one hour, furnace cooled.
6a	6	High-carbon steel	226	N, 790° C. 15 minutes, air cooled; A, 790° C., cooled in furnace.
6b	6	do	695	N, 790° C. 15 minutes, air cooled; OQ, 790° C.; T, 260° C. one hour, cooled in air.
8a	8	Nickel steel	179	A, 815° C. one hour, cooled in furnace.
8b	8	do	454	815° C. one-half hour, quenched in water.
9a	9	do	167	A, 760° C. one hour, cooled in furnace.
9b	9	do	502	760° C. one-half hour, quenched in water.
10a	10	Monel metal	261	Tested as received (hard drawn).
10b	10	do	150	A, in charcoal at 760° C. one hour, cooled in furnace.
11a	11	Piano wire, No. 2	490	Tested as received.
12a	12	Oil-tempered wire, No. 2	511	Do.
13a	13	High-carbon steel	211	N, 790° C. 15 minutes, air cooled; A, 790° C. 30 minutes.
13b	13	do	708	N, 790° C. 15 minutes, air cooled; OQ, 790° C.; T, 260° C. one hour.
14a	14	Phosphor bronze	210	Held at 100° C. for 24 hours.
15a	15	do	248	Do.
16a	16	Nickel silver	250	Do.
17a	17	do	240	Do.
18a	18	do	212	Do.
18b	18	do	890	A, 800° C. two hours, furnace cooled.
19a	19	do	268	Held at 100° C. for 24 hours.
20a	20	do	272	Do.
21a	21	do	233	Do.
22a	22	Stainless steel (KA2)	488	Tested as received (hard drawn).
22b	22	do	195	Tested as received (annealed).
23a	23	do	462	Tested as received (hard drawn).
23b	23	do	176	Tested as received (annealed).
24a	24	Stainless steel (Enduro A)	306	Tested as received (hard drawn).
24b	24	do	168	Tested as received (annealed).
25a	25	Stainless steel (Enduro AA)	273	Tested as received (hard drawn).
25b	25	do	184	Tested as received (annealed).
26a	26	Stainless steel No. 12	328	Tested as received (hard drawn).
26b	26	do	190	Tested as received (annealed).
27a	27	Duralumin	120	Tested as received (age hardened).
29a	29	Silico-manganese steel	281	A, 870° C. one hour, furnace cooled; N, 855° C. one-half hour, air cooled.
29b	29	do	418	A, 870° C. one hour, furnace cooled; N, 855° C. one-half hour; T, 510° C. 40 minutes, cooled in air.
30a	30	Brass	238	Tested as received (hard drawn).
31a	31	Elinvar		Tested as received.
32a	32	Modulvar		Do.
33a	33	Tungsten		Do.
34a	34	Beryllium bronze	291	Hard drawn; age hardened 228° C. 3 hours, air cooled.

A=annealed. N=normalized. OQ=oil quenched. T=tempered.

In the cases where the spring is listed as having been "tested as received," the springs were coiled at room temperature from the wire as received and were subjected to no heat treatment. No detailed information is available relative to the heat treatment or cold work of the wires other than that given in the table. A number of the springs were subjected to a temperature of 100° C. to relieve trapped stresses produced in winding the spring. In every case the heat treatment refers to that given the coiled springs.

In general, it was planned to make tests on the springs when the material was in the most favorable condition as to heat treatment or cold work from the viewpoint of its use as an elastic element. In most cases data were also obtained on the spring in the annealed condition.

4. EXPERIMENTAL PROCEDURE AND RESULTS

(a) EXPERIMENTAL PROCEDURE

For the purpose of determining the extensions X_1 and X_2 of the installed springs an auxiliary knife-edge balance was used to support lever L (fig. 2) at its center. The cap ordinarily supporting the lever L was lowered and then the deflections of the platforms K_1 and K_2, for various weights on the auxiliary balance, were measured by means of micrometers. These readings were plotted against the loads on the auxiliary balance and the resulting curve for each spring was extrapolated in order to determine the reading at zero load. The latter reading was determined in this manner before and after each experiment while the springs were at room temperature.

Before subjecting the springs to the temperature cycle, the auxiliary balance was disengaged and the springs were extended a desired amount by raising the screw cap on the center rod L. The readings of the micrometers in contact with K_1 and K_2 for this position of the lever arm and those for the zero position as above determined sufficed to give the initial extensions X_1 and X_2 of the auxiliary and test springs, respectively.

To guard against errors arising from elastic after working, the drift, or the change with time of the deflection of the springs at room temperature, was observed with the optical lever system. In most cases the springs tested showed very small or no relative drift, but when the relative drift was initially large, sufficient time was allowed for the rate to decrease to a small value.

The change in the deflections of the two springs during the temperature cycle was obtained by means of the two optical levers. In this cycle the auxiliary spring was maintained at +30° C. while the temperature of the test spring was changed from +50° to −50° C. and back to +50° C. The temperature during a measurement was held constant within 0.5° C. The temperature of the auxiliary spring was determined by means of a mercurial thermometer, the bulb of which was in the bath near the midportion of the spring. The temperature of the test spring was determined by means of two calibrated liquid-in-glass thermometers with the bulbs placed in the bath at points near the upper and lower ends of the spring. The average of the readings obtained before and after every observation on the change of deflection of the springs was taken as the temperature of the test spring. The temperature of one test spring was also determined during a temperature cycle by means of two thermocouples which were soldered to the

spring, one at the top and the other at the bottom. The results by the two methods agreed within 0.5° C. throughout the range from +50° to −50° C.

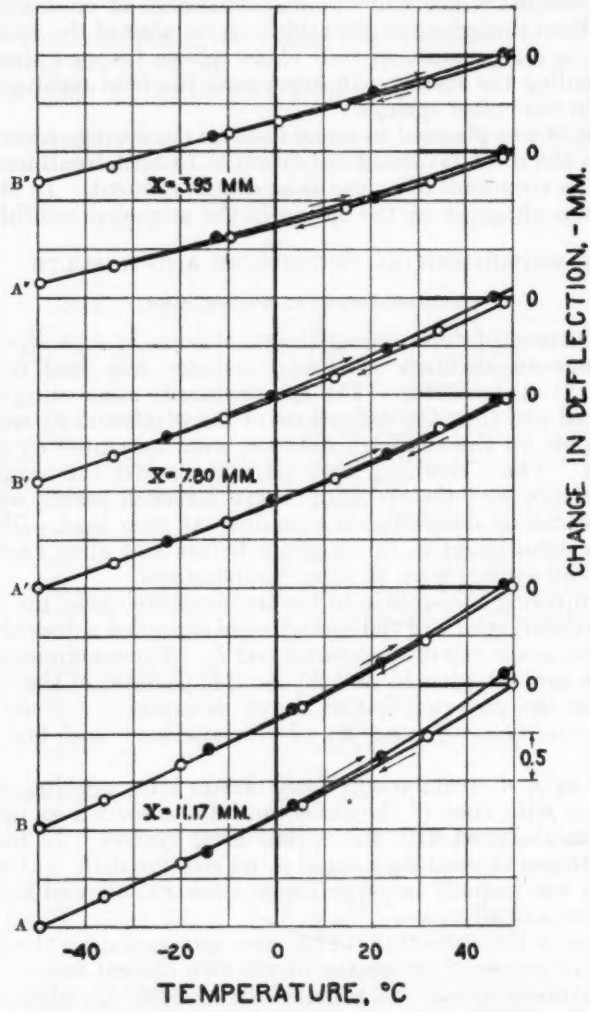


FIGURE 5.—*Change in deflection of spring No. 23a with change in temperature*

The optical lever above the test spring gave the data shown in curves *B*, *B'*, and *B''* and the optical lever above the auxiliary spring that in curves *A*, *A'*, and *A''* with the sign of the ordinate reversed.

(b) CORRECTIONS APPLIED TO THE READINGS

During the temperature cycle to which the test spring was subjected, which was almost invariable from +50° to −50° C. and then back to +50° C., the temperature of other parts of the apparatus also changed with consequent changes in dimensions which in some cases contributed to the observed deflections. The source and amount

of these extraneous deflections were determined with considerable care and their effect eliminated from the results. These parts were (*a*) the central invar rod and the caps (*E* and *Q*, fig. 2), and (*b*) the system of rods which support the mirror M_2.

(c) METHOD OF REDUCING THE DATA

The method of reducing the data was essentially the same in all cases and is most conveniently presented by giving the details of the reduction for a typical case. The data obtained experimentally on spring No. 23a (stainless steel *KA*2) are shown graphically in Figure 5. The ordinates represent the change x in the initial deflection and the abscissas the corresponding temperatures of the test spring. The deflections for temperatures decreasing are represented by open circles and those for temperatures increasing, by filled circles. The deflections obtained by means of the optical mirror above the auxiliary spring for mean initial deflections of the springs of 11.17, 7.80, and 3.95 mm are given, with signs reversed, in the curves marked *A*, *A'*, *A''*, respectively, and those obtained above the test spring, corrected for the thermal expansion of the supports of the optical lever, are given by curves *B*, *B'*, and *B''*.

For most materials the points for increasing and decreasing temperature fell on the same curve within very close limits, but for spring No. 23*a* (fig. 5) two distinct curves were obtained. In all cases like the latter, the points midway between the two curves were used to evaluate the slope $\frac{dx}{d\theta}$ (equation (7)). The medians of the curves in Figure 5 may be regarded, within the errors of observations, as arcs of circles. Hence if we draw two straight lines, one joining the two points of the arc corresponding to $+50°$ and 0° C., and the other joining the points corresponding to 0° and $-50°$ C., the slopes of these two lines will give the value of $\frac{dx}{d\theta}$ at the temperatures $+25°$ and $-25°$ C. On this basis the following values were derived from Figure 5.

Rate of change of deflection $\frac{dx}{d\theta}$

X	Curves A	Curves B	Average
mm	*mm/°C.*	*mm/°C.*	*mm/°C.*
3.95	0.00157	0.00143	0.00150
7.80	.00226	.00217	.00221
11.17	.00293	.00282	.00288
	$\theta=-25°$ C.		
3.95	0.00118	0.00130	0.00124
7.80	.00180	.00177	.00178
11.17	.00227	.00228	.00228

These average values of $\frac{dx}{d\theta}$ at $+25°$ and $-25°$ C. are plotted in Figure 6 against X, the mean initial deflection of the springs. The points fall on straight lines within the error of the experiments. Each line in the figure is made to pass through a point, the coordinates of

which are the mean values of X and of $\frac{dx}{d\theta}$, and is drawn so that it appears to the eye to have the least deviation from the experimental points. The intersection of these lines with the axis of the ordinates

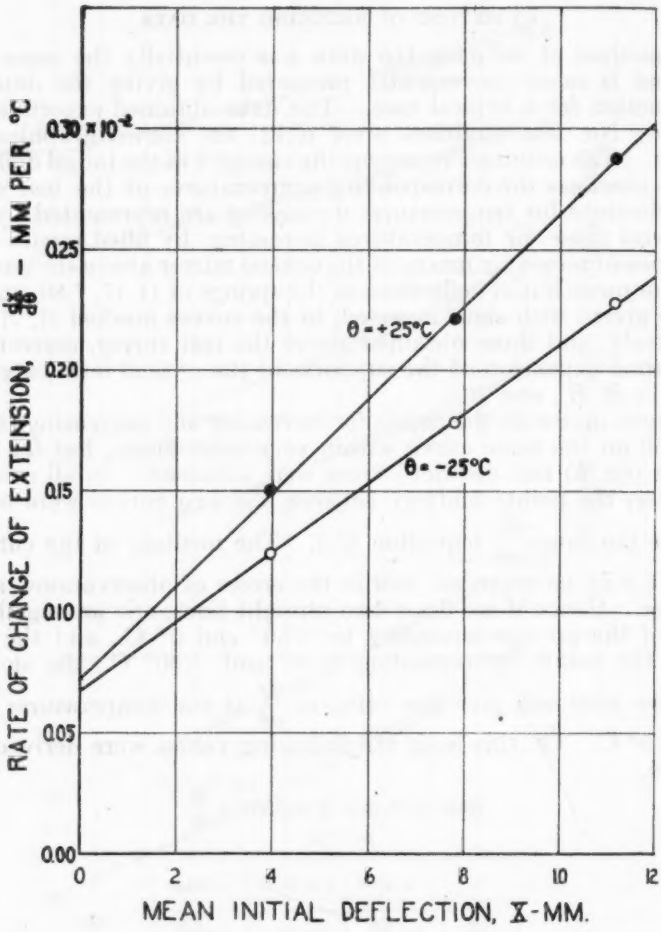


FIGURE 6.—*Relation of the rate of change in the extension,* $\frac{dx}{d\theta}$, *of the spring No. 23a with temperature to the mean initial extension X of the springs*

gives the values of $\frac{dx_0}{d\theta}$, one of the quantities in the working formula, equation (7). The following quantities were obtained from Figure 6.

Temperature	$X=10$mm $\frac{dx}{d\theta}$	$X=0$ $\frac{dx_0}{d\theta}$	$\frac{2}{X}\left(\frac{dx}{d\theta}-\frac{dx_0}{d\theta}\right)$ $\times 10^3$ per °C.
°C.	mm/°C.	mm/°C.	
+25	0.00265	0.00073	38.4
−25	.00211	.00068	28.6

The thermal coefficient of expansion α of this alloy is stated to be 1.6×10^{-5}. Hence, using the working formula (7), the temperature coefficient m is found to be

$$m_{25}=-40.0\times10^{-5} \text{ per °C.}$$

$$m_{-25}=-30.2\times10^{-5} \text{ per °C.}$$

The average of the above values is -35.1×10^{-5} which is m_0, the coefficient at 0° C. The ratio of two coefficients m_{25}/m_{-25} is 1.32.

(d) EXTENSION AT ZERO TENSION

It was seen in Figure 6 that the straight lines through the observed points cut the axis of the ordinates at two points the mean ordinate of which is $+70\times10^{-5}$ mm per °C. This is the rate of deflection for the case of initial zero tension.

If the change in deflection with temperature at initial zero tension is due only to the expansion of the parts, it can be shown that

$$x_0=\frac{c+l}{1+S_1/S_2}$$

where c is the sum of the expansions of the parts exterior to the test spring (a_2 and b_2, fig. 1) and l that of the test spring. It follows that

$$\frac{dx_0}{d\theta}=\frac{\frac{dc}{d\theta}+\frac{dl}{d\theta}}{1+S_1/S_2} \tag{9}$$

The contraction c of the spring assembly extending from the base plate to the lever arm L (fig. 2), but exclusive of that of the test spring, was determined when the temperature of the bath was changed from +50° to −50° C. To determine this the test spring was replaced by a rod of phosphor bronze for which the thermal coefficient of expansion was known. While the temperature of the auxiliary spring was maintained constant, the change in its deflection was observed at a number of temperatures of the phosphor bronze rod in the range from +50° to −50° C. From these deflections, together with the known contraction of the phosphor bronze rod and the previously determined contraction of the central rod, the contraction c was evaluated and found to be linear with temperature. Four determinations gave a mean value for $\frac{dc}{d\theta}$ of $(56\pm2)10^{-5}$ mm per °C. Tests showed that $\frac{dc}{d\theta}$ did not differ sufficiently from the above value in the two branches of the temperature cycle to justify the use of separate values.

The value of $\frac{dx_0}{d\theta}$, computed from equation 9 is $+94\times10^{-5}$ mm per °C. for the stainless steel spring for which data are given in Figures 5 and 6. The quantity $\frac{dc}{d\theta}$ was computed on the basis of a thermal coefficient of expansion of 1.6×10^{-5} per °C., and a length of spring

of 8.1 cm. The quantity $\frac{dc}{d\theta}$ has the value given above and S_1/S_2 is 0.96. There is a difference of 24×10^{-5} mm per °C. between the above computed value of $\frac{dx_0}{d\theta}$ and the average of the two values obtained from Figure 6. Since experimental errors and the possibility that too high a value of the temperature coefficient of expansion was used account only for a small part of the difference, this particular test spring had a contraction during the temperature cycle other than that which can be evaluated on the basis of pure thermal expansion.

A similar comparison of the two determinations of $\frac{dx_0}{d\theta}$ was made for all of the other springs. For springs shaped from hard-drawn material the above discussed difference proved to be as large as 28×10^{-5} mm per °C. On the other hand, for springs which were annealed or heat treated after being shaped from the material in the "as-received" condition, the difference was smaller than 6×10^{-5} mm per °C.

(e) EXPERIMENTAL RESULTS

The values obtained for the temperature coefficient m_0 of the modulus of rigidity at 0° C. of the various springs tested are given in Table 3. In addition, the heat treatment, the maximum shear stress, the ratio $\frac{m_{25}}{m_{-25}}$ and the value of the thermal coefficient of expansion α used in evaluating m are given for each spring.

The temperature coefficient m_0 is for all practical purposes the average coefficient for the temperature range $-50°$ to $+50°$C. A measure of the variation of the coefficient with temperature is given by the ratio $\frac{m_{25}}{m_{-25}}$.

The values of the maximum shear stress given in Table 3 were computed from the formula

$$f=\frac{2Lr}{a^3}$$

in which f is the maximum stress to which the specimen was subjected at its maximum extension, L is the force producing the maximum extension, and r and a are the radii of the coils and wire, respectively. These stresses are all within the proportional limit.

(f) ACCURACY OF RESULTS

The sources of experimental error are as follows:

1. Uncertainty in the amount of the initial deflection of the springs, and therefore in the quantity X. A comparison of the values of the deflections obtained before and after the temperature cycle shows that the difference was in no case more than 2 per cent, and in most cases

TABLE 3.—*Temperature coefficients of the elastic moduli*

(The temperature coefficients of the modulus of rigidity and modulus of elasticity are, respectively, m and e, the subscripts of which denote the temperatures in degrees centigrade at which the values were determined. The coefficients m_0 and e_0 are also the average values in the temperature range −50° to +50° C.)

Spring No.	Materia	Heat treatment	Coefficient of thermal expansion $\alpha\times10^6$	$m_0\times10^5$	$\frac{m_{25}}{m_{-25}}$	Maximum shear stress	$e_0\times10^6$	$\frac{e_{25}}{e_{-25}}$	$(m_0-e_0)\times10^6$
						Lbs/in.²			
1a	Chromium vanadium steel	T	1.17	−26.2	1.12	9,500	−26.3	1.13	−0.1
1b	do	A	1.17	−25.5	1.19	9,200	−25.5	1.07	0
8a	Nickel steel, 5 per cent Ni	A	1.05	−27.5	1.16	8,800	−28.4	1.06	−.9
8b	do	T	1.05	−27.3	1.16	8,800	−26.0	1.10	1.3
9a	Nickel steel, 3½ per cent Ni	A	1.04	−27.1	1.14	7,500	−27.0	1.08	.1
9b	do	T	1.04	−26.2	1.12	7,000	−27.1	1.09	−.9
22a	Stainless steel (KA2), 0.14 per cent C	H. D.	1.64	−43.6	1.25	9,400	−43.2	1.13	.4
22b	do	A	1.6	−39.9	1.31	6,800	−39.7	1.16	.2
23a	Stainless steel (KA2), 0.05 per cent C	H. D.	1.6	−35.4	1.35	9,400	−37.9	1.19	−2.5
24a	Stainless steel (Enduro A)	H. D.	.99	−27.2	1.23	9,600	−26.6	1.10	.6
24b	do	A	.99	−25.5	1.13	8,600	−28.6	1.06	−3.1
25a	Stainless steel (Enduro AA)	H. D.	.99	−26.7	1.24	8,800	−25.9	1.04	.8
25b	do	A	.99	−25.7	1.12	9,500	−27.3	1.15	−1.6
26a	Stainless No. 12	H. D.	1.04	−28.3	1.12	7,900	−25.6	1.12	2.7
26b	do	A	1.04	−25.5	1.09	9,200	−27.0	1.13	−1.5
29a	Silico-manganese steel	A	1.1	−22.8	1.09	7,700	−24.5	1.12	−1.7
29b	do	T	1.1	−23.0	1.21	7,900	−25.1	1.14	−2.1
6a	High-carbon steel No. 10	A	1.1	−22.5	1.19	8,200	−20.1	1.12	2.4
6b	do	T	1.1	−27.1	1.12	7,600	−26.0	1.07	1.1
13a	High-carbon steel	A	1.1	−21.8	1.12	9,100	−19.3	1.12	2.5
13b	do	T	1.1	−27.3	1.09	4,100	−26.2	1.11	1.1
4a	Piano wire, No. 1	R	1.1	−25.9	1.11	10,500	−27.1	1.06	−1.3
4b	do	A	1.1	−20.1	1.10	8,500	−20.7	1.14	−.6
11a	Piano wire, No. 2	R	1.1	−26.0	1.09	10,700	−26.7	1.10	−.7
5a	Oil tempered wire, No. 1	R	1.1	−27.1	1.11	10,900	−25.9	1.10	1.2
5b	do	A	1.1	−24.3	1.20	9,200	−24.0	1.09	.3
12a	Oil tempered wire, No. 2	R	1.1	−27.8	1.19	9,600	−25.4	1.05	2.4
3a	Phosphor bronze	H. D.	1.7	−41.1	1.02	4,400	−38.0	1.02	3.1
14a	do	H. D.	1.7	−38.5	1.02	5,400	−40.0	1.06	−1.5
15a	do	H. D.	1.7	−40.0	1.02	4,400	−36.0	1.05	4.0
16a	Nickel silver, 10 per cent Ni	H. D.	1.8	−37.1	1.02	4,800	−34.6	1.06	2.5
17a	Nickel silver, 14 per cent Ni	H. D.	1.8	−37.8	1.02	5,500	−34.7	1.03	3.1
18a	Nickel silver, 19 per cent Ni	H. D.	1.8	−37.7	1.02	6,400	−34.8	1.06	2.9
19a	Nickel silver, 10 per cent Ni	H. D.	1.8	−39.1	1.02	5,300	−37.9	1.03	1.2
20a	Nickel silver, 15 per cent Ni	H. D.	1.8	−38.8	1.02	5,900	−34.5	1.07	4.3
21a	Nickel silver, 18 per cent Ni	H. D.	1.8	−37.3	1.02	8,200	−35.2	1.05	2.1
18b	Nickel silver, 19 per cent Ni	A	1.8	−34.4	1.02	4,500	−33.0	1.05	1.4
27a	Duralumin	A. H.	2.3	−55.1	1.02	3,400	−58.3	1.12	−3.2
10a	Monel metal	H. D.	1.3	−32.2	1.10	6,300	−29.7	1.02	2.5
10b	do	A	1.3	−30.0	1.09	8,000	−29.5	1.12	.5
30a	Brass, 73.0 per cent Cu	H. D.	1.8	−38.8	1.02	4,100	−38.9	1.17	−.1
31a	Elinvar	H. D.	.6	−7.2	------	6,500	−6.6	------	.6
32a	Modulvar	H. D.	.0	------	------	------	+48.2	------	------
33a	Tungsten	R	.4	−6.6	------	33,100	−9.5	------	−2.9
34a	Beryllium bronze, 1.9 per cent Be	A. H.	1.7	−33.4	1.02	4,800	−35.0	1.06	−1.6

T = Tempered.
A = Annealed.
H. D. = Hard drawn.
R = As received.
A. H. = Age hardened.

less than 1 per cent. Errors of the same amount are thus introduced into the value of the temperature coefficient m_0.

2. Uncertainty in the measured values of the temperature of the springs. Tests showed the temperatures to be correct within 0.5° C. (See Sec. II, 4, on Experimental Procedure and Results, p. 299.)

3. The possibility that the contraction of a given test spring and its supports during a temperature cycle depends upon the deflection of the spring as well as the temperature. If this contraction depends

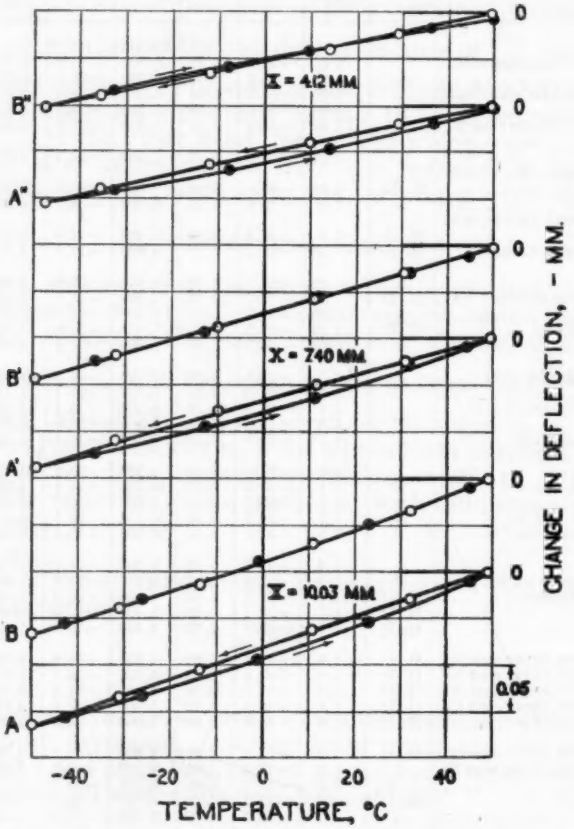


FIGURE 7.—*Change in deflection of spring No. 6a with change in temperature*

The optical lever above the test spring gave the data shown in curves B, B', and B'', and the optical lever above the auxiliary spring that in the curves A, A', and A'' with the sign of the ordinate reversed.

upon the deflection of the spring the error from its neglect in determining the temperature coefficient will not be in excess of 2 per cent.

4. Possible error in the value of the coefficient of expansion of the sample materials. As this coefficient enters only as a second order correction term (equation (7)) large percentage errors in the value used will introduce only negligible errors in the final results.

Thus, any one determination of the temperature coefficient of rigidity m_0 may be in error by an amount as large as 4 per cent.

In the determination of the ratio $\frac{m_{25}}{m_{-25}}$ the principal source of error was that in some cases the changes in deflection x, were observed to be different for decreasing and increasing temperatures. For example in Figure 7, showing the data obtained on spring No. 6a, the points for decreasing temperature as measured with the mirror above the auxiliary spring fall practically on a straight line, whereas the points for increasing temperature fall on a curve. In this and similar cases the mid line was used to represent the data. Although it is clear that m_0 obtained from the mid line is not open to an error larger than above stated, the same can not be said for the determinations of the ratio $\frac{m_{25}}{m_{-25}}$. The error in cases where the ratio is approximately unity will not exceed the 4 per cent above mentioned, otherwise it is likely to be larger, but is estimated not to exceed 10 per cent.

III. TEMPERATURE COEFFICIENT OF YOUNG'S MODULUS OF ELASTICITY

1. DERIVATION OF THE WORKING FORMULA

The apparatus used in the measurement of the temperature coefficient of Young's modulus of elasticity is shown in Figure 8. Only a description sufficient to explain the derivation of the working formula will be given here. The lower ends of the two springs s_1 and s_2, called, respectively, the auxiliary and the test springs, are attached to the separate bases, B_1 (not shown in the figure) and B_2, which are held fixed by suitable supports. Both of these springs are immersed in liquid temperature control baths.

By a process analogous to that followed in the derivation of the working formula for the temperature coefficient of the modulus of rigidity, we find

$$\frac{1}{S_2'}\frac{dS_2'}{d\theta} = -\frac{2}{\Phi}\left(\frac{d\phi}{d\theta} - \frac{d\phi_0}{d\theta}\right) \tag{10}$$

where Φ is the mean of the absolute values of the initial twists of the two springs, ϕ and ϕ_0 are, respectively, the changes with temperature θ in the angular deflection of the test spring for an initial twist Φ_2 and for zero initial twist, and S_2' is the stiffness of the spring with regard to angular deflection. The quantities ϕ and ϕ_0 are measured from the position when the test spring is at $+50°$ C. and the temperature of the auxiliary spring held constant, and taken as positive when the curvature of the coils of the test spring increases. The quantity Φ is positive when the initial twist of the test spring is such as to increase the curvature of its coils.

In terms of the constants of a helical spring the angular stiffness S' is

$$S' = \frac{\pi r^4 E}{4L}$$

where E is the Young's modulus of elasticity, r is the radius of the wire, and L is the length of the wire. This can also be represented for a given spring by

$$S' = \beta L^3 E \tag{11}$$

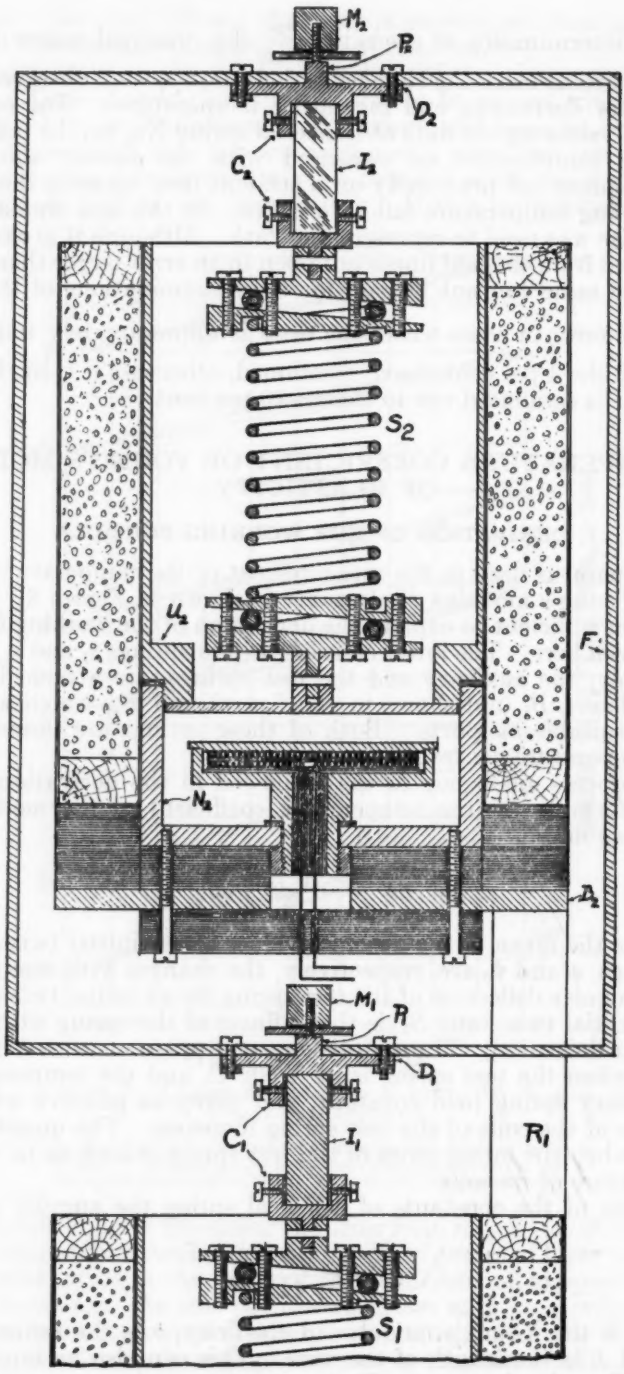


FIGURE 8.—*Cross-sectional diagram of the apparatus for the determination of the temperature coefficient of Young's modulus of elasticity*

(See the text for the meaning of the letters.)

where β is a numerical constant and L has the dimensions of length. β is unaffected by the temperature if the ratio of r to L is invariant with temperature. Differentiating equation (11) with respect to θ, and then dividing by equation (11) we obtain

$$\frac{1}{S'}\frac{dS'}{d\theta}=\frac{1}{E}\frac{dE}{d\theta}+3\alpha \tag{12}$$

where α is the temperature coefficient of linear expansion. After making the obvious substitution in equation (10) there results

$$\frac{1}{E}\frac{dE}{d\theta}=-\frac{2}{\Phi}\left(\frac{d\phi}{d\theta}-\frac{d\phi_0}{d\theta}\right)-3\alpha \tag{13}$$

Let

$$e=\frac{1}{E}\frac{dE}{d\theta} \tag{14}$$

Equation (13) is the working formula for the experiments. The quantity e is defined as the temperature coefficient of Young's modulus of elasticity. The quantities $\frac{d\phi}{d\theta}$ and $\frac{d\phi_0}{d\theta}$ are the rates of change of the angular deflection of the test spring corresponding, respectively, to the mean of the absolute values and to the zero value of the initial deflections Φ_1 and Φ_2 of the springs.

2. DESCRIPTION OF THE APPARATUS

Figures 8 and 9 show a cross-sectional diagram and a photograph of the apparatus for measuring the temperature coefficient of Young's modulus. In Figure 8 the complete assembly is shown only for the upper spring. The construction of the lower spring assembly is the same as that of the upper. The base plates (B_2, fig. 8), which hold firmly the circular cups (N_2), are bolted to two vertical rigid rods. Only one of the rods, R_1 is shown in the diagram, but both may be seen in Figure 9. The construction of the baths U_1 and U_2 and the lower connections of the springs s_1 and s_2 is similar to that in the apparatus for determining the temperature coefficient of the rigidity modulus of springs of heavy wire. Special clamps C_1 and C_2 terminating in circular disks D_1 and D_2 with central projections P_1 and P_2 are attached to the upper connections of the springs. The midportions of the clamps, I_1 and I_2 are square in cross section and one, I_2, is made of glass in order to obtain better temperature insulation. The springs after being given the initial deflection, are interconnected by frame F which is sufficiently strong so as not to suffer appreciable distortion. Each of the disks D_1 and D_2 has 18 perforations circularly distributed near the edge, to facilitate the clamping to the frame F.

An optical system consisting of the mirrors M_1 and M_2, telescopes and scales, was used for measuring the angular deflection of each spring. There were two mirrors at both M_1 and M_2, inclined 90° to each other. The scales were placed at such distances from each mirror so that a rotation of one degree of arc gave a change in reading of 2 cm on the scale. Readings on the scale were estimated easily to tenths of a millimeter.

3. MATERIALS

The same springs were used to determine the temperature coefficients of both of the elastic moduli. These are described, together with the chemical composition and heat treatment, in the section on the temperature coefficient of the modulus of rigidity.

4. EXPERIMENTAL PROCEDURE AND RESULTS

(a) EXPERIMENTAL PROCEDURE

The test procedure was very similar to that followed in the experiments for determining the temperature coefficient of the rigidity modulus including the method of measuring and controlling the temperature of the springs. Similarly, the temperature of the auxiliary spring was maintained constant at +30° C. and that of the test spring varied in a cycle from +50° to −50° C. and back to +50° C. At various points in the cycle the change in deflection of both springs was measured by means of the optical system.

(b) METHOD OF REDUCING THE DATA

The method followed in reducing the experimental data will be presented by giving an example, using the data for high carbon steel spring No. 9b, given in Figure 10. Here the ordinates represent twice the change ϕ in the initial deflection Φ and the abscissas the temperature of the test spring. The open circles represent deflections observed at decreasing temperatures of the test spring and the filled circles, deflections at increasing temperatures. The mean initial deflections of the test spring, measured at room temperature, about 25° C., were 92.0°, 12.5°, −8.1°, and −87.5°.

The lines through the observed points are not straight and may be regarded as arcs of circle. Hence, if the slopes of the two straight lines, one joining points on the arc at 0° and 50° C., and the other joining the points at 0° and −50° C., are determined, we obtain, respectively, the quantity $\frac{2d\phi}{d\theta}$ at the temperatures 25° and −25° C. The results of such determinations for the curves in Figure 10 are:

Initial deflection	$2\frac{d\phi}{d\theta}$	$2\frac{d\phi}{d\theta}$
Degrees	*Degrees per ° C. θ=25° C.*	*Degrees per ° C. θ=−25° C.*
92.0	0.0242	0.0215
12.5	.0036	.0024
−8.1	−.0025	−.0020
−87.5	−.0225	−.0200

These values of $2\frac{d\phi}{d\theta}$ for 25° and −25° C. are plotted against Φ in in Figure 11. The points for each temperature lie on a straight line within experimental errors. Each line is made to pass through a point whose coordinates are the means of coordinates of the plotted points and is so drawn that its deviation from these points appears by eye to be a minimum. The intersection of these lines with the axis

FIGURE 9.—*Apparatus for the determination of the temperature coefficient of Young's modulus of elasticity*

UNIV. OF MICH.

of the ordinates gives the value of $2\frac{d\phi}{d\theta}$. The following quantities are read from the graph:

Temperature	Φ	$2\frac{d\phi}{d\theta}$	Φ	$2\frac{d\phi}{d\theta}$
° C.	Degrees	Degrees per ° C.	Degrees	Degrees per ° C.
+25	100	0.0260	0	0
−25	100	.0230	0	0

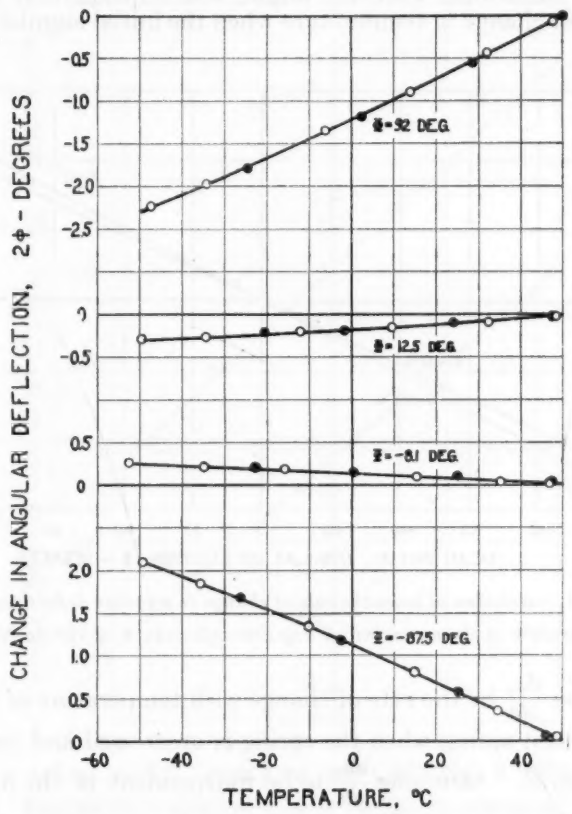


FIGURE 10.—*Effect of change in temperature of test spring on the angular deformation Φ of spring No. 9b*

The thermal coefficient of expansion α of this material is 1.1×10^{-5}. Inserting the above values into the working formula, equation (13) gives -29.3×10^{-5} at $+25°$ C. and -26.3×10^{-5} at $-25°$ C. for the temperature coefficient e of Young's modulus of elasticity. The value at 0° C. is the average of these values or $e_0=-27.8\times10^{-5}$ per ° C. The ratio of the values at $+25°$ and $-25°$ C. is

$$\frac{e_{25}}{e_{-25}}=1.13$$

The mean value Φ of the absolute values of the initial angular deflections of the two springs at 25° C. is used in evaluating e_{-25} and e_{25} without the introduction of sensible error.

(c) EFFECT OF TEMPERATURE AT INITIAL ZERO ANGULAR DEFLECTION

The rate of change of angular deflection is plotted in Figure 12 against the mean initial angular deflection for springs of oil-tempered steel (No. 5a). The straight line *A* represents the results of the tests on this spring when prepared from the original tempered material without subsequent heat treatments. It meets the axis of the ordinates at a point other than the origin, which means that this spring deflects with change in temperature when the initial angular deflection

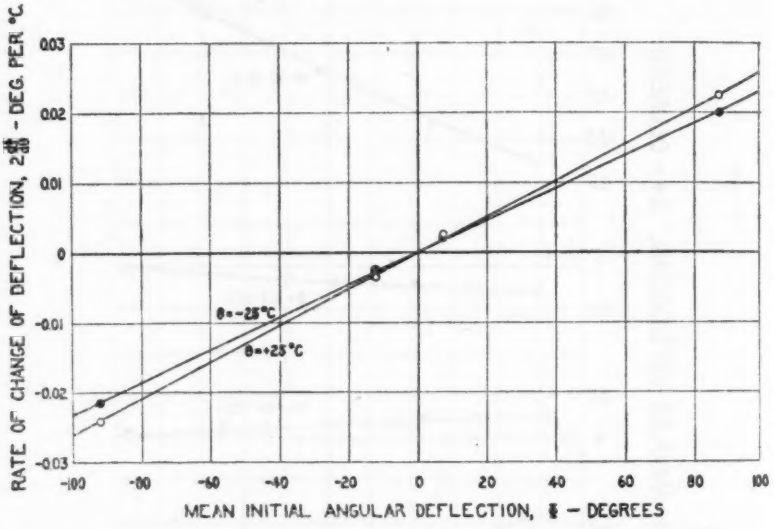


FIGURE 11.—*Relation of twice the rate of change in angular deflection* $\frac{2d\phi}{d\theta}$ *with temperature to the mean initial angular deflection* Φ *of spring No. 9b*

is zero. Let $\frac{d\psi_0}{d\theta}$ be the rate of change with temperature of the deflection of the test spring when the spring is unstressed and entirely free of the clamp *C*. Assuming $\frac{d\psi_0}{d\theta}$ to be independent of the deflection Φ it can be shown that $\frac{d\psi_0}{d\theta} = (1 + S_1'/S_2') \frac{d\phi}{d\theta}$. Calculated by means of this formula, in which S_1'/S_2' is assumed to be unity and $\frac{d\phi_0}{d\theta}$ is obtained from the graph, the rate of change of twist $\frac{d\psi_0}{d\theta}$ is 0.020 degree per °C.

To show that this rate of change of deflection at zero angular deflection actually occurs the test spring was disengaged from the clamp and its deflection measured as the temperature was varied.

The following results were obtained, which are in satisfactory agreement with value given above.

Temperature of the spring	Degree of twist per °C.
°C.	
+15	0.022
+8	.022
−16	.021
−24	.021

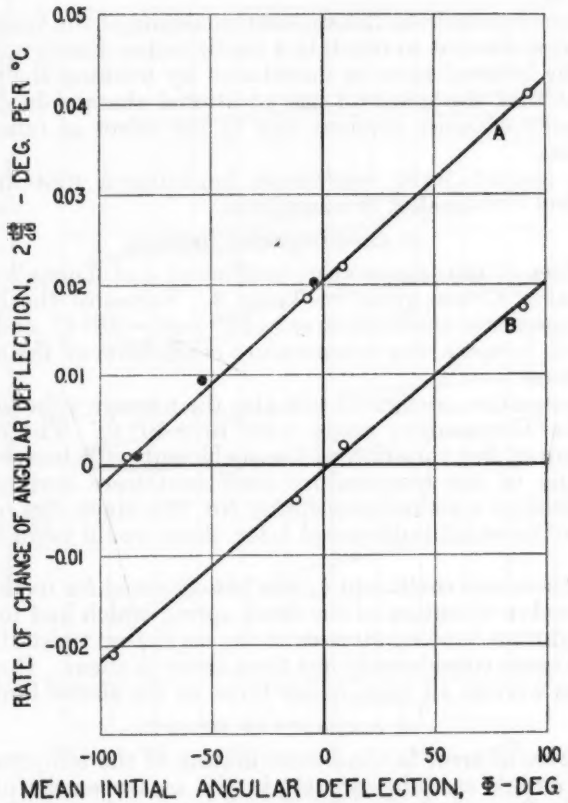


FIGURE 12.—*Relation of twice the rate of change in angular deflection* $\frac{2d\phi}{d\theta}$ *with temperature to the mean initial angular deflection* Φ *of the springs No. 5a and 5b*

Data represented by the line *A* were obtained with the springs shaped from the oil-tempered wire. The test spring shows twist at zero deformation. Data represented by the line *B* were obtained with the springs annealed after shaping

To show that $\frac{d\psi_0}{d\theta}$ is substantially constant for all values of the deflection of the spring the following experiment was performed. The auxiliary and test springs were initially twisted in opposite directions by amounts $\Phi_1 = -83°$ and $\Phi_2 = +83°$ and clamped. The tempera-

tures of both of the springs were varied as a unit starting from a common temperature. There was a consequent twist of 0.020° per °C. which is in good agreement with the results previously obtained.

The deflection with temperature at the initial zero angular deflection is relatively large for steel springs which were not heat treated after being wound.

For springs heat treated after winding this effect was practically zero which is shown in a striking way by curve *B* in Figure 12 which represents the data obtained after annealing spring No. 5a. The fact that $\frac{d\psi_0}{d\theta}$ is here practically zero suggests that this deflection with temperature results from the stressed condition of the spring material. Probably it is due not so much to a modification during a temperature cycle of the internal stresses introduced by working the material, as to the fact that the material has additional changes in deflection in the internally stressed portions due to the effect of temperature on the modulus.

Springs shaped from nonferrous hard-drawn materials show a similar effect but smaller in magnitude.

(d) EXPERIMENTAL RESULTS

The values of the temperature coefficient e of Young's modulus of elasticity at 0° C. are given in Table 3. Values of the ratio e_{25}/e_{-25} of the temperature coefficients at +25° and −25° C. and the difference m_0-e_0 between the temperature coefficients of the two moduli are also given.

The temperature coefficient e_0 is also the average value of the coefficient in the temperature range −50° to +50° C. The ratio e_{25}/e_{-25} is a measure of the variation of the coefficient with temperature.

No values of the temperature coefficient were derived from the data obtained on stainless steel spring No. 23b, since, due to the anomalous behavior which is discussed later, these would be of little significance.

The temperature coefficient e_0 was not obtained for modulvar owing to the excessive vibration of the small spring which had to be used.

The maximum bending stresses at the maximum twist of the springs were in all cases considerably less than those in shear. Consequently, the stresses were in all cases below those at the elastic limit.

(e) ACCURACY OF RESULTS

The sources of error in the determination of the temperature coefficient of Young's modulus are (1) in the measurement of the mean initial deflection of the auxiliary and test springs and (2) in the measurement of temperature of the springs. For the great majority of the springs the error in determining the initial deflection was within 1 per cent and in all cases the error in the temperature was within 1° C. Thus, not considering the possible error in the value of the thermal coefficient of expansion, the error in the coefficient does not exceed 2 per cent.

The error in the ratio of the temperature coefficient at +25° C. to that at −25° C. is principally due to the difference in the angular deflection of the spring for decreasing and increasing temperatures. This difference in deflection was very much less than in the case of the experiments to determine the temperature coefficient of the modulus of rigidity and therefore the errors are substantially less.

IV. DISCUSSION

1. ANOMALOUS BEHAVIOR OF STAINLESS STEEL

The behavior of annealed stainless steel (KA2) spring No. 23b containing 0.05 per cent carbon, is very unusual compared with those

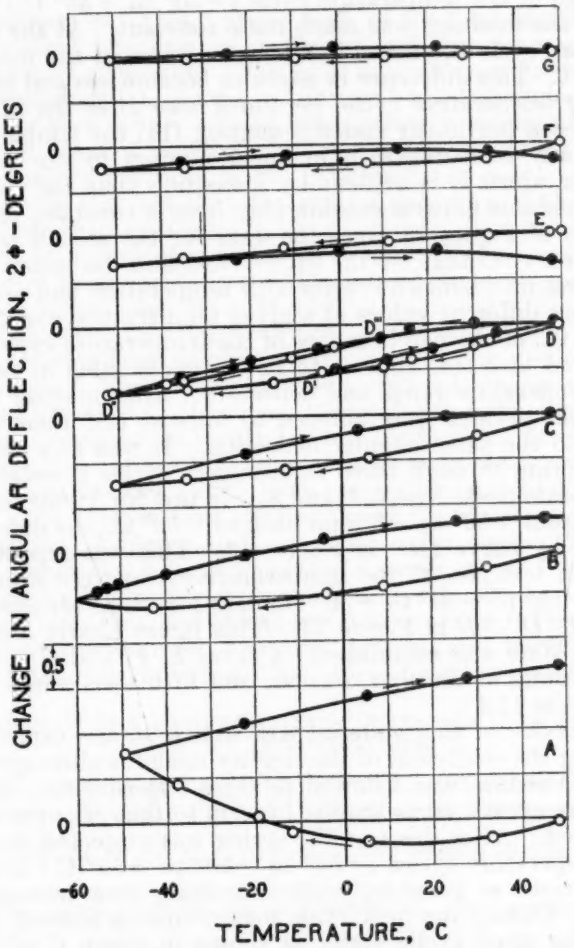


FIGURE 13.—*Effect of temperature on the angular deflection of a spring (No. 23b) of annealed stainless steel*

Each group of curves *A*, *B*, and *C* and *E*, *F*, and *G* are the results of the first, second, and fifth test for an initial angular deflection (Φ) of 41.6 for the first group and 11.4° of arc for the second. Curves *D* were obtained after three temperature cycles for an initial angular deflection of 41.6°, and shows the spring to be in the cyclic state. The open circles represent observations made in the decreasing temperature part and the solid circles in the increasing temperature part of the cycle.

of other materials. The results of some of the tests are shown in Figure 13.

The change in angular deflection as a function of the temperature is given in Figure 13. Before obtaining these data the springs were given an average angular deflection of 42° and the differential drift

noted which after a period of time became less than 0.02° per hour. The test spring was then subjected to the usual temperature cycle and the change in deflection measured, obtaining the values shown in curve *A* (fig. 13). As the temperature was decreased from +50° C. the modulus first increases and then decreases, while during the returning half of the temperature cycle (−50° to +50° C.) the rate of change of the modulus was much more constant. At the end of this temperature cycle the metal had a lower value of the modulus than at the start. This difference in modulus became less and less for each succeeding temperature cycle, becoming zero after the fifth cycle.

As has been previously stated (equation (14) the temperature coefficient at any temperature is in linear relation to the slope of this curve from which it is evident by inspection that the coefficient of Young's modulus departs considerably from a constant value.

Curve *B* of Figure 13 gives the data for the second temperature cycle and curve *C* that for the fifth. Notice in the latter curve that the temperature coefficient varies with temperature and also that the modulus has different values at a given temperature, except at +50° and −50° C., in the two branches of the temperature cycle. Further tests showed that this appears to be the cyclic state of the material for this temperature range and deflection. After making test No. 5, curve *C*, the springs were allowed to untwist and then were again retwisted to the same angular deflection. It was now necessary to pass the spring through three temperature cycles to establish again the cyclic state (tests Nos. 6, 7, and 8). In test No. 10 the temperature cycle was from +50° to +5° and back to +50° C., the data for which are shown by curve *DD′* in Figure 13. This was repeated in test No. 11. In test No. 12 the temperature cycles were from +50° to −50° to +10° to −50° to +50° C., data for which are shown by the curves *DD″ D″ ′ D* in Figure 13. This figure clearly shows that a true cyclic state was established. Curves *E*, *F*, and *G* in Figure 13, give the results of the first, second, and fifth tests when the initial deflection was 11.4°.

The behavior of this material was similar in the experiments for determining the coefficient of the rigidity modulus although a slightly different procedure was followed in these experiments. In the first temperature cycle a curve similar in form to that of curve *A* (fig. 13) was obtained. After this test the spring was subjected to three successive temperature cycles (+50° to −50° to +50° C.) in as short a period of time as possible, without making measurements of the deflection. During the next cycle measurements showed the spring to be in the same cyclic state, as shown in curve *C* of Figure 13 which was obtained as a result of tests which took a definitely much longer time to make. Since the cyclic state was obtained independently of time it is concluded that the behaviour is mainly an effect due to change in the constitution with temperature and not of elastic afterworking.

The effect was obtained only to a slight degree with stainless steel spring No. 24b which is in agreement with the negative result of cold treatment obtained by Luerssen and Green [2] with a sample of approximately the same composition, especially as to the carbon content. The difference in behavior of springs 23b and 24b appears to be

[2] G. V. Luerssen and O. V. Green, Trans. Am. Soc. Steel Treat., vol. 19, p. 501, 1932.

caused by the difference in the carbon content, respectively, 0.05 and 0.14 per cent, which seems to be reasonable according to the work of Krivobok and Gensamer.[3]

2. RELATIVE VALUES OF THE TEMPERATURE COEFFICIENTS

An inspection of Table 3 shows that, of the pure metals, tungsten has the smallest temperature coefficient and also the smallest coefficient of thermal expansion. This is in accordance with the modification of Wertheim's law given by Andrews,[4] which includes as a corollary, that for pure metals, a small temperature coefficient of elasticity and a small thermal coefficient of expansion are associated. The relatively large differences in the coefficients m and e for tungsten may be due to the fact that the crystal structure of the wires was fibrous rather than isotropic.

With the exception of stainless steel KA2, elinvar, and modulvar, it is seen that the temperature coefficients of the steels vary within a rather small range, from 19 to 27×10^{-5}.

Modulvar, which has practically the same composition as invar, is known [5] to have a large positive coefficient which is confirmed by the present results. The values for the sample of elinvar were rather higher than expected.[5] However, the material is known to require careful heat treatment to obtain the low coefficient. It was not heat treated after the cold work incidental in forming the spring.

The two stainless steels KA2, with carbon contents of 0.14 and 0.05 per cent, have temperature coefficients of the elastic moduli which are considerably higher than those of the other steels. These steels also have higher thermal coefficients of expansion.

Of the group of nonferrous materials, duralumin has the largest temperature coefficient and Monel metal the smallest. The coefficients of the nickel silvers, brass, phosphor bronze, and beryllium bronze differ but littel from those found for copper by other investigators.

3. VARIATION OF THE TEMPERATURE COEFFICIENTS OF THE MODULI WITH TEMPERATURE

The coefficients m_0 and e_0 given in Table 3 are also with but negligible error the average values of the coefficients for the temperature interval $-50°$ to $+50°$ C. Although the values of the ratios $\frac{m_{25}}{m_{-25}}$ and $\frac{e_{25}}{e_{-25}}$ are open to question in some cases, they are even in these cases of value as an indication of the variation of the temperature coefficients with temperature. Very roughly, but sufficiently accurate for many purposes, the ratio

$$\frac{m_0}{m_{-50}} = \frac{m_{50}}{m_0} = \frac{m_{25}}{m_{-25}}$$

and similarly for the coefficients of Young's modulus.

The coefficients in all cases increase in absolute value with increasing temperature. For the materials, phosphor bronze, nickel silver, and

[3] V. N. Krivobok and M. Gensamer, Trans. Am. Inst. Min. and Metall. Eng., Iron and Steel Div., p. 325, 1931.
[4] J. P. Andrews, Phil. Mag., series 6, vol. 50, p. 665, 1925.
[5] P. Chevenard, Travaux et Memoires de Bur. Int. des Poid et Mes., vol. 17, 1927.

brass, all containing copper, the rate of increase is not as large as in steel, duralumin, and Monel metal. For some of the stainless steels the coefficients appear to increase at a greater rate than for other steels.

For high-carbon steels (spring Nos. 6a, 6b, 13a, and 13b) the average value

$$\frac{m_{25}}{m_{-25}}=1.13 \text{ and } \frac{e_{25}}{e_{-25}}=1.11$$

Tomlinson's expression[6] for the relation between the rigidity modulus of iron and temperature for the temperature range 0° to 100° C. gives 1.11 for the above ratio of the torsion moduli when extrapolated to −25° C. Dadourian's expression[7] for the relation of Young's modulus of steel and temperature for temperatures above 0° C., gives 1.29 for the ratio of the modulus at +25° C. to that at −25° C.

4. TEMPERATURE COEFFICIENT OF POISSON'S RATIO

Grüneisen[8] in an important paper on the compressibility of isotropic elastic materials has deduced the relations

$$\text{I. } m>e>\gamma$$

$$\text{II. } m-e=\frac{G\eta}{3}(e-\gamma)$$

$$\text{III. } \frac{1}{\sigma}\frac{d\sigma}{d\theta}=\frac{1+\sigma}{\sigma}(m-e)$$

where σ is Poisson's ratio, η the compressibility and the thermal coefficient of compressibility. The first relation is based on the assumption that compressibility, as well as Poisson's ratio, increases with temperature. The second and third relations result from the isotropic character of elastic materials.

The value of the quantity $\frac{G\eta}{3}$ is known to be a small fraction, different for various materials, but always lying between the limits one-sixth and one-twelfth. The above relations are very useful as they afford us a means of knowing how large the difference between the two temperature coefficients of the moduli can be.

When, with the first Grüneisen relation in mind, the two coefficients m and e are compared it is found that, except in a few cases, $m-e$ is positive, and also that the difference is larger for nonferrous material than for the steels.

Restricting our consideration to the steels, it may be inferred, because of Grüneisen's second relation, that either the thermal coefficient of Poisson's ratio for steels at 0° C. is zero or a very small quantity. Bock's[9] results on the direct determination of Poisson's ratio of hardened English steel by Kirchoff's method and for a temperature

[6] H. Tomlinson, Proc. Roy. Soc., vol. 40, p. 343, 1886.
[7] H. M. Dadourian, Phil. Mag., vol. 42, p. 442, 1921.
[8] E. Grüneisen, Ann. d. Phys., vol. 33 (338), p. 1239, 1910.
[9] A. Bock, Wied. Ann., vol. 52, p. 609, 1894.

range, 20° to 150° C., may be represented by the following expression—

$$1{,}000\sigma = 255.6 + 0.019\theta + 0.00009\theta^2$$

from which we find for the thermal coefficient of Poisson's ratio at 0° C.

$$\frac{1}{\sigma}\frac{d\sigma}{d\theta} = 7 \times 10^{-5}$$

Using Grüneisen's third relation this gives the value 2×10^{-5} for the difference $m - e$ which agrees with the results for high-carbon steels given in Table 3.

Katzenelsohn,[10] Schaefer,[11] and Angenheister,[12] among the earlier observers, have determined both of the quantities m and e from experiments made on the same specimen. Although they find m to be larger than e, Grüneisen has remarked that with these observers the difference $m - e$ was too large to be compatible with his second relation, particularly for results on materials of high melting points. Goens,[13] among recent observers, has determined these quantities for aluminum and brass by a new method from the same specimen of each material. The difference $m - e$ obtained by him for brass is of the same order of magnitude as that in the present investigation.

5. EFFECT OF HEAT TREATMENT ON THE TEMPERATURE COEFFICIENTS OF THE ELASTIC MODULI

The coefficients of the elastic moduli of high-carbon steels (springs 6a, 6b, 13a, and 13b, Table 3) are affected very definitely by heat treatment. The coefficients of the annealed specimens are about 20 per cent less than those for the tempered specimens. It is significant that annealing brings the value of the coefficients very near to the value found by other experimenters for iron. Coefficient e_0 for iron was found by Geons [14] to be -21.3×10^{-5}; by Katzenelsohn[15] -22.3×10^{-5}; by Thomas [16] -19.4×10^{-5}. For iron Tomlinson [17] found m_0 to be -24.4×10^{-5}; Guye and Fredericksz [18] -21.3×10^{-5}.

In alloys steels, however, the effect of heat treatment is not very definite; differences that were found were of the same order as the errors of experimentation. The results for chromium-vanadium steel do not contradict those of Brombacher and Melton [19]; the results on nickel steel agree with those of Kimball and Lovell.[20]

Among the nonferrous materials one spring of the nickel-silver group was tested in the as-received condition and also after annealing. Annealing produced, as is seen from the Table 3, a decrease of about 10 per cent in the value of the coefficients, which is a decrease of the same order as found by Brombacher and Melton. In the case of Monel metal the decrease was less than that found for nickel silver.

---

[10] N. Katzenelsohn, Inn. Diss. (Berlin), 1887.
[11] C. Schaeffer, Ann. d. Phys., vol. 5 (310), p. 220, 1901.
[12] G. Angenheister, Ann. d. Phys., vol. 11 (316), p. 188, 1903.
[13] E. Goens, Ann. d. Phys., vol. 4 (396), p. 733, 1930.
[14] See footnote 13, p. 319.
[15] See footnote 10, p. 319.
[16] Paul A. Thomas, Dissertation, (Jena), 1899.
[17] See footnote 6, p. 318.
[18] C. E. Guye and V. Fredericksz, Compt. Rend., vol. 149, p. 1066, 1909.
[19] See footnote 1, p. 290.
[20] A. L. Kimball, jr., and D. E. Lovell, Phys. Rev., vol. 26, p. 121, 1925.

V. CONCLUSIONS

The temperature coefficient of the modulus of rigidity and of the modulus of elasticity of a number of metals and alloys have been determined in the temperature range $-50°$ to $+50°$ C. The coefficients were obtained in so far as possible on each material in the condition of heat treatment or cold work most suitable for its use as a spring or diaphragm and also in the annealed condition. The experimental results are presented in Table 3.

It is shown that Grüneisen's three relations between the temperature coefficients and Poisson's ratio were in general confirmed by these data.

The temperature coefficients were found, for the most part, to be dependent, to a significant extent, on the heat treatment and cold work of the material.

Except for tungsten the percentage difference in the two temperature coefficients was sufficiently small so that for practical purposes they may be taken as equal.

The coefficients, in general, varied with temperature. The average value for the temperature interval $-50°$ to $50°$ C. is that for $0°$ C. given in Table 3.

The coefficients are independent of external stress within the maximum stress at which the springs were tested.

VI. ACKNOWLEDGMENTS

The Aluminum Co. of America, the American Steel & Wire Co., the International Nickel Co., the Seymour Manufacturing Co., the Phosphor Bronze Smelting Co., the Beryllium Development Corporation, the Wallace Barnes Co., and the Cuyahoga Steel & Wire Co. cooperated by furnishing special materials for use in this investigation.

We are greatly indebted to Dr. W. G. Brombacher for valuable assistance, especially in the preparation of the manuscript, and to F. Cordero for his suggestions in the design of the apparatus.

WASHINGTON, September 10, 1932.

A MAGNETIC BALANCE FOR THE INSPECTION OF AUSTENITIC STEEL

By Raymond L. Sanford

ABSTRACT

The paper describes an experimental model of a magnetic balance for measuring the attractive force between a permanent magnet and a specimen of austenitic steel with which it is in contact. Experiments with this model indicate that such an instrument should be of considerable practical value for the inspection of corrosion-resistant austenitic steel in view of the fact that the magnetic permeability has been found to be a good index of the resistance to corrosion of this type of material. The instrument is portable and can be applied to different parts of a completed structure.

CONTENTS

	Page
I. Introduction	321
II. Description of the instrument	322
III. Experimental results	323
IV. Interpretation of results	325

I. INTRODUCTION

In austenitic steel the iron exists in the nonmagnetic or gamma phase. In plain carbon steels this phase is stable only at high temperatures, but it can be retained at ordinary temperatures when the iron is alloyed with proper proportions of certain other elements. Chromium and nickel are among the most important of these elements. In recent years some types of austenitic steel have come into extensive use, primarily on account of their property of corrosion resistance. As corrosion tests are usually tedious and time consuming, and yield results which are frequently difficult to interpret with certainty, efforts have been made to discover whether or not some other more easily determined property can be used as an index of the resistance to corrosion. The property which appears to give the greatest promise for this purpose is the magnetic permeability. In addition to serving as an index of corrosion resistance, the permeability is of importance in cases where the material is to be used in proximity to a magnetic compass.

It is a simple matter to determine the magnetic permeability by well-known ballistic methods when specimens of the material can be prepared in suitable form. These methods are obviously unsuited, however, to the testing of various parts of a completed structure in place. The desirability of such tests arises from the fact that the austenitic structure may be partially decomposed as a result of the treatment applied in the process of construction. Decomposition of the austenite may be brought about also by severe service conditions,

such as high temperature and by mechanical working during fabrication. As a result of the breakdown of the austenitic structure the alpha or more familiar phase of iron forms resulting in reduced resistance to corrosion and an increase in magnetic permeability.

The practical value of a portable instrument for inspecting the various parts of a completed structure of austenitic steel in terms of magnetic permeability was first brought to the attention of the writer by P. E. McKinney, metallurgical engineer of the Bethlehem Steel Co. It was at his suggestion that the development of such an instrument was undertaken.

A consideration of several possible types of measurement, together with the results of preliminary experiments, led to the conclusion that the most promising method was by a measurement of the force of attraction between the specimen and a permanent magnet in contact with its surface. In order to try out this method, an experimental instrument was designed and constructed. In view of the satisfactory performance of this instrument, it is described below in the belief that such an instrument with only minor modifications can be used to advantage for the inspection of austenitic corrosion-resistant steel.

II. DESCRIPTION OF THE INSTRUMENT

Figure 1 is a photograph of the instrument. An astatic pair of magnets is clamped in a pivoted holder carried in jewel bearings. The motion of this pivoted system is limited by an adjustable stop. The lower end of the magnet which comes in contact with the specimen is ground to a hemispherical form to facilitate good reproducibility. The force of attraction between the magnet and the specimen is measured in terms of the torque of a helical spring of phosphor bronze. One end of this spring is clamped to the pivoted mounting and the other to a spindle coaxial with the pivots. The torque is measured by means of a graduated dial which indicates the angle through which the spring is twisted.

Although the actual dimensions of the various component parts are of relatively minor importance, there are certain conditions which must be fulfilled if satisfactory performance is to be obtained. The magnetic element must be astatic, the center of gravity of the moving system must be on the axis of rotation, and the friction in the bearings must be small.

If a single magnet were to be used the torque due to the reaction of the earth's field on the magnet would introduce an error in the readings. This error would vary in magnitude with the orientation of the magnet with respect to the direction of the earth's field. In order to obviate this error, two magnets of equal strength are used. They are inserted in the holder with like poles together so that the resultant torque, due to the earth's field, is zero. The magnets employed in the experimental instrument are of cobalt magnet steel, 5 cm long and 5 mm in diameter.

Since the instrument is intended to be used in other positions than with the base horizontal, there should be no torque due to gravity. In the present instrument this condition is not exactly met. The center of gravity is slightly below the axis of rotation when the base is horizontal. This gives a difference between readings obtained on the same specimen when the base is horizontal and when it is vertical.

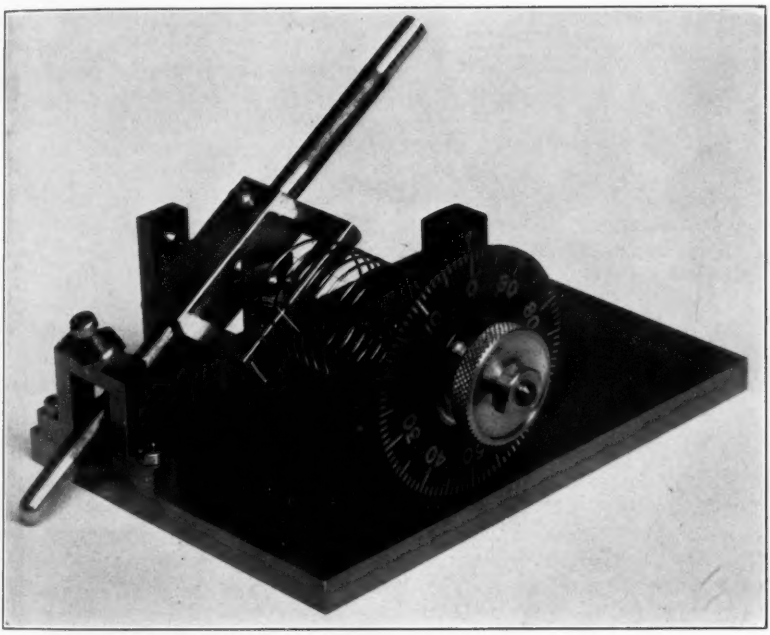


FIGURE 1.—*Experimental magnetic balance*

This discrepancy could be obviated by providing suitable means for mechanically balancing the system.

The requirement as to pivot friction is obvious. In an attempt to make the instrument as rugged as possible, the bearings were first made of hardened steel. The friction in these bearings was excessive, being augmented by magnetic attraction due to proximity to the strong poles of the magnets. The substitution of phosphor bronze did not remedy the trouble and finally sapphire bearings and steel pivots were put in. This eliminated excessive friction, but resulted in a somewhat less rugged instrument.

The particular form of spring used was chosen on account of the ease with which variations in strength can be obtained. Several springs were made using different sizes of wire, diameter of coil, and winding pitch. A more compact instrument would result from the use of a flat spiral spring but, for the present purpose, the form employed proved to be very satisfactory.

The dial is 4 cm in diameter and has 100 scale divisions. It is held in position on its shaft by a friction washer which facilitates the adjustment of the zero.

In use, the instrument is placed with its base flat upon the specimen so that the lower end of the magnet comes in contact. The spring is then twisted until the torque is just sufficient to pull the magnet away from the specimen. The torque required is measured in terms of the angle through which the spring is twisted as indicated by the dial reading. The springs used with the present instrument have torque constants ranging from 0.45 g-cm per division to 2.6 g-cm per division. Obviously care must be taken to avoid injury to the pivots and jewels, but with reasonably careful handling such an instrument should be sufficiently rugged for practical use.

III. EXPERIMENTAL RESULTS

In order to investigate the relationship between the readings of the instrument and the magnetic properties of the material, a series of 31 specimens of corrosion-resistant steel was selected from a large number of samples of unknown source and composition which had previously been submitted for test. The maximum permeability of these specimens as determined by the ballistic method ranged from less than 1.01 to 5.31, usually occurring at a magnetizing force of 200 oersteds (gilberts per centimeter). Preliminary tests with the magnetic balance showed a fairly definite relation between the balance readings and maximum permeability, but the discrepancies were sufficiently large and numerous to call for more detailed investigation. Two points were of particular interest, namely, the value of magnetizing force applied to the material under test and the effect of previous magnetic treatment on the results. In the course of the experiments the degree of homogeneity of the material was also found to be an important factor.

The question of the applied magnetizing force was attacked in two different ways, neither one of which gave an entirely satisfactory answer. In an attempt to determine the value of the magnetizing force directly, the total flux emanating from the hemispherical end of the permanent magnet was measured by means of a test coil and ballistic galvanometer. The average flux density was then calcu-

lated by dividing the total flux by the area of the surface of the hemisphere. The magnetizing force thus determined was approximately 900 oersteds. Since the magnetizing force did not exceed 300 oersteds in the previous ballistic tests, new determinations were made at higher magnetizing forces up to 1,000 oersteds. A comparison of the balance readings with the values of permeability at a magnetizing force of 900 oersteds revealed discrepancies fully as great as the comparison with the values of maximum permeability.

The second way in which an attempt was made to find out the effective value of magnetizing force applied by the balance consisted in plotting the balance readings against the permeability corresponding to various values of magnetizing force as determined ballistically. In no case was a better correlation found than that between the

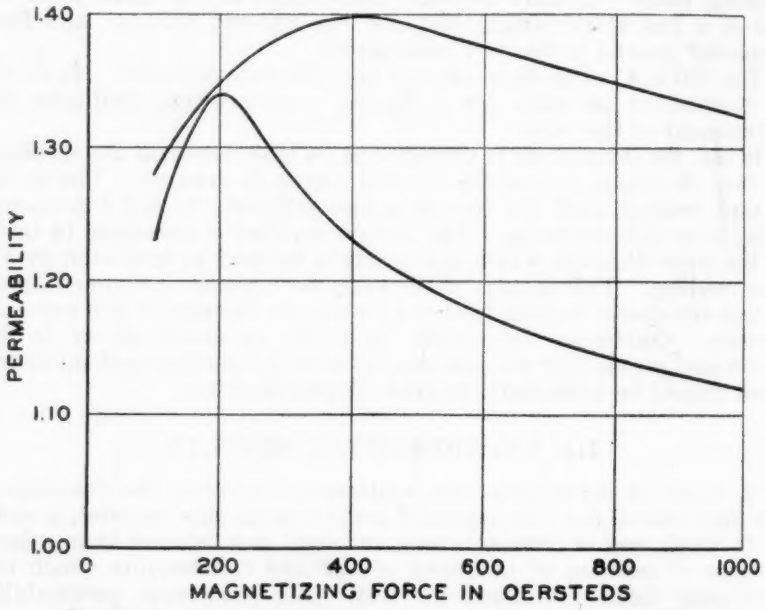


FIGURE 2.—*Permeability curves for two specimens of austenitic steel*

balance readings and the values of maximum permeability. These results should probably be expected since the force of attraction is a function not only of the magnetization of the specimen at the point of contact, but also of the magnetization in the immediate vicinity. The different elements of the volume of the material involved would, of course, be subjected to the influence of magnetizing forces of different magnitudes, and the observed mechanical force would be the integrated effect of the whole volume involved. For this reason, it is not proper to consider that the balance actually measures the permeability corresponding to any single value of magnetizing force.

The ballistic tests brought out the fact that the materials varied not only with regard to maximum permeability, but also in the relation between permeability and magnetizing force. This is illustrated by Figure 2 in which curves for samples Nos. 16 and 18 are shown. Although the permeability of the two materials is nearly the

same at a magnetizing force of 200 oersteds, it is obvious that they are magnetically quite different. The balance readings for these two specimens were 22.0 and 18.5, respectively.

In the course of the experiments, it was found that the readings obtained were in many cases affected to an appreciable extent by previous magnetic treatment. The reading at a given point, for example, might be changed by several divisions by rubbing the magnet of the balance over the surface of the specimen near the point at which the measurement was made. The effect is most noticeable for the materials of higher permeability. However, if the specimens are demagnetized before a reading and care is taken to avoid rubbing the balance magnet over the surface when placing it in position, readings can be repeated within half a division. Passing one pole of a small electromagnet energized with alternating current over the specimen effectively removes the effect of previous magnetization.

Differences in the degree to which various specimens are affected by previous magnetization are easily explained by the different amounts of magnetic hysteresis exhibited. Observations of coercive force taken from a maximum magnetizing force of 1,000 oersteds gave values ranging from 43 to 178 oersteds. There was no relationship between the coercive force and permeability. The differences in magnetic characteristics would seem to indicate that the materials differ not only in the amount of ferromagnetic material present, but also in its distribution within the structure. The relationships involved might quite profitably be made the subject of further investigation.

Another factor which must be taken into consideration is the degree of uniformity of the specimens. In several cases it was found that, even when care was taken to eliminate the effect of previous magnetic history, readings taken at various points on the surface of the specimen showed differences considerably in excess of the allowable experimental error. Although this introduces an additional difficulty in connection with the calibration of the instrument, the ability to reveal such variations in the material is an important feature.

IV. INTERPRETATION OF RESULTS

Figure 3 shows the relation between the readings of the magnetic balance and the permeability as determined by the ballistic method at a magnetizing force of 200 oersteds. Although there is evidently a very good correlation, especially for the lower values of permeability, it should be borne in mind that the balance actually measures nothing but the mechanical force of attraction between the magnet and the specimen. This force is an integrated effect involving a considerable range of magnetizing force. Since the actual scale readings are functions not only of the magnetic properties of the specimens, but also of the strength of the magnet and of the spring, each individual instrument will have a calibration constant which must be determined by taking readings on a series of specimens whose magnetic properties are known. In many cases, it will be necessary to determine only a certain critical scale reading as the upper limit for satisfactory material. For routine inspection an instrument with a fixed spring tension might prove most satisfactory. For other applications, it would be better to have the dial, so that quantitative values of the attractive force could be obtained.

In the light of the results obtained with the experimental model it seems reasonable to conclude that an instrument of this type would be of considerable practical value for the investigation and testing

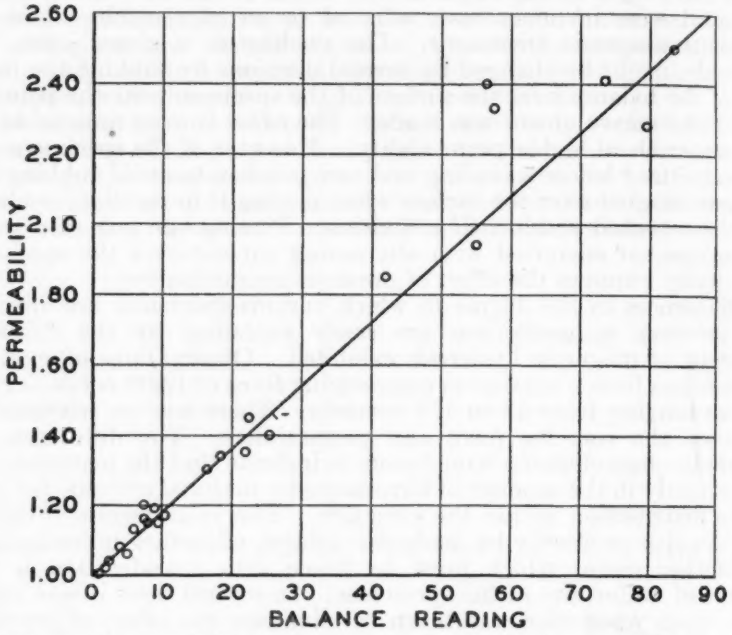


FIGURE 3.—*Correlation between balance readings and permeability at a magnetizing force of 200 oersteds*

of austenitic corrosion-resistant steels and other materials having the same range of values of permeability.

WASHINGTON, December 5, 1932.

DETERMINATION OF ALUMINUM IN NITRIDING STEELS BY THE USE OF 8-HYDROXYQUINOLINE

By H. A. Bright and Robert M. Fowler

ABSTRACT

A rapid method for the determination of aluminum in nitriding steels is described. The procedure consists in (*a*) separating aluminum from most of the iron by precipitating with sodium bicarbonate, (*b*) dissolving this precipitate in acid and precipitating the rest of the iron with sodium hydroxide, (*c*) treating the filtrate with 8-hydroxyquinoline to precipitate aluminum, and (*d*) either titrating with a standard solution of potassium bromate and potassium bromide after dissolving the aluminum quinolate in acid, or weighing the quinolate after drying at 135° C. The bicarbonate and sodium hydroxide precipitations and the determination of aluminum by 8-hydroxyquinoline are discussed briefly.

CONTENTS

	Page
I. Introduction	327
II. Discussion of the method	328
1. Precipitation of aluminum by sodium bicarbonate	328
2. Separation of aluminum from iron and nickel by precipitation with sodium hydroxide	329
3. Determination of aluminum by the use of 8-hydroxyquinoline	331
III. Recommended procedure	332

I. INTRODUCTION

Practically all types of nitriding steels contain aluminum as a major alloying constituent, the amounts varying from 0.25 to 2 per cent. The "Nitralloy" type, containing 0.60 to 1.2 per cent of aluminum, 0.8 to 1.3 per cent of chromium, and 0.15 to 0.25 per cent of molybdenum, is perhaps the one most widely used. Special grades of nitriding steels may also contain 0.5 to 1.0 per cent of vanadium, 0.10 to 2.5 per cent of nickel and 7 per cent or more of chromium. The Bureau of Standards' standard sample No. 106 contains 1.06 per cent of aluminum (total), 0.017 per cent of aluminum present as Al_2O_3, 1.29 per cent of chromium and 0.16 per cent of molybdenum. At the bureau the aluminum content of the standard was found by using a slight modification of a method of analysis described by Cunningham (3).[1] In this method most of the iron is removed by the Rothé ether method, the remaining iron separated with cupferron, the filtrate boiled with nitric and perchloric acids to oxidize chromium and destroy organic matter, the aluminum precipitated twice with ammonium hydroxide and the ignited and weighed oxide corrected for impurities. This method, while very accurate, requires considerable time and hence is not suitable for rapid commercial determinations. Precipitation with 8-hydroxyquinoline (1, 4), after suitable separations, seemed to

[1] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

offer promise of more rapid and sufficiently accurate determinations. A method of analysis based on this principle is described in one of the following sections. The procedure consists in (*a*) separating aluminum from manganese and most of the iron and nickel by precipitating with sodium bicarbonate; (*b*) dissolving the precipitate in acid and precipitating chromium and the rest of the iron and nickel with sodium hydroxide; (*c*) precipitating aluminum in the filtrate with 8-hydroxyquinoline in a slightly ammoniacal solution containing tartrate and hydrogen peroxide, whereby aluminum is separated from molybdenum, vanadium, tin, phosphorus, and small amounts of chromium (which escaped the sodium hydroxide separation), and (*d*) either titrating with a standard solution of potassium bromate and potassium bromide after dissolving the aluminum quinolate in acid, or weighing the quinolate after drying at 135° C. By this method duplicate determinations of aluminum that are accurate to ± 0.02 per cent of the sample can be made in about three hours. Certain experimental data relating to the several separations upon which the method is based are presented before giving the detailed description of the recommended procedure.

II. DISCUSSION OF THE METHOD

1. PRECIPITATION OF ALUMINUM BY SODIUM BICARBONATE

Precipitation with bicarbonate has been used successfully in procedures for the determinations of chromium, vanadium, manganese, and small amounts of aluminum in steels (6). Its suitability for steels of relatively high aluminum content, such as aluminum bearing steels, has been somewhat in doubt because of uncertainty as to the conditions that must be established to insure complete precipitation. In the bicarbonate precipitation, it is desirable to use the minimum amount of bicarbonate, as an unnecessary excess increases the amount of iron precipitated.

The data given in Table 1 were obtained by dissolving 4 g portions of steel in dilute sulphuric acid, adding various amounts of solutions of aluminum and chromium sulphate, and then adding different quantities of an 8 per cent solution of sodium bicarbonate. The aluminum in the precipitate was determined by the Cunningham method already outlined in the introductory section. Experiments 1 and 2 demonstrate that 0.05 ml of the bicarbonate solution per 1 mg of aluminum in excess of the amount required to form a permanent precipitate is not enough for complete precipitation. The term "excess bicarbonate" is used throughout this article to denote the amount of bicarbonate added after the first permanent precipitate is obtained. Experiments 3 to 9 indicate that an excess of 0.13 to 0.18 ml of bicarbonate per 1 mg of aluminum sufficies for complete precipitation in plain steels and in chromium steels containing no more than 3 per cent of chromium. If this excess is used about 0.2 g of iron is precipitated. It should be mentioned in passing that it is desirable to filter and wash the bicarbonate precipitate as soon as it has settled. Exposure to air causes oxidation of ferrous iron and consequent precipitation of ferric hydroxide by hydrolysis. This reaction tends to lower the pH of the solution, though it is not known whether the slight increase in acidity would cause some resolution of aluminum hydroxide.

TABLE 1.—*Data on the precipitation of aluminum by sodium bicarbonate in the presence of ferrous iron*

[4 g of steel used in each experiment]

Experiment No.	Steel [1]	Other elements added	Al present or added	Aluminum found	Error	Excess $NaHCO_3$ added	
						Per mg of Al	Total
		g	*g*	*g*	*mg*	*ml*	*ml*
1	16b		0.0756	0.0564	−19.2	0.05	4.0
2	16b		.0756	.0526	−23.0	.05	4.0
3	16b		.0756	.0746	−1.0	.11	8.5
4	16b		.0756	.0756	.0	.13	10.0
5	55		.0376	.0377	+.1	.16	6.0
6	16b		.0378	.0382	+.4	.16	6.0
7	16b		.0378	.0375	−.3	.16	6.0
8	55		.0400	.0398	−.2	.18	7.0
9	55	0.120 Cr	.0400	.0404	+.4	.18	7.0
10	55	.367 Cr	.0400	.0387	−1.3	.18	7.0
11	55	.420 Cr	.0400	.0388	−1.2	.23	9.0
12	55	.550 Cr .250 Ni	.0400	.0400	.0	.35	14.0
13	55	.550 Cr .250 Ni	.0400	.0398	−.2	.35	14.0

[1] Percentage compositions of the steels used are as follows: 16b, basic open hearth, C=1.01, Mn=0.38, P=0.025, Si=0.08, Ni=0.003, Cr=0.007, V=0.004, Al=0.008, Sn=0.001; 55, ingot iron, C=0.013, P=0.003, Si=−0.001, Ni=0.020, Cr=0.002, Al=0.002, Sn=0.008.

With high-chromium steels a larger excess of bicarbonate is needed, for it is apparently necessary to precipitate a considerable part of the chromium before all of the aluminum is precipitated. This is in accord with the hydrolysis curves for aluminum and chromium published by H. T. S. Britton (2). Experiments 12 and 13 show that an excess of 0.35 ml of bicarbonate per 1 mg of aluminum suffices for high-chrome steels.

Nickel divides in the bicarbonate separation. With high-nickel steels about 10 per cent of nickel remains in the precipitate. In steels of low-nickel content, the percentage retained is higher. For example, with 250 mg of nickel present, the bicarbonate precipitate contained approximately 30 mg of nickel whereas with 8.5 mg about 5 mg of nickel was retained.

Experiments 4, 6, and 7 show that organic matter which may be formed when a high-carbon steel is dissolved in a nonoxidizing acid does not prevent complete precipitation of aluminum in the bicarbonate procedure.

2. SEPARATION OF ALUMINUM FROM NICKEL AND IRON BY PRECIPITATION WITH SODIUM HYDROXIDE

It has been stated that separations of aluminum are incomplete if precipitations are made with sodium hydroxide in solutions containing bivalent or trivalent nickel (5, 9). H. A. Buchheit, of the Bureau of Standards, in tests (unpublished) on the separation of 0.05 g of aluminum from 0.10 g of nickel by means of a double precipitation with sodium hydroxide, found that approximately 14 mg of aluminum was retained in the second sodium hydroxide precipitate in the case of bivalent, and 5 mg in the case of trivalent nickel. Additional tests were made by the authors to ascertain the amount

of aluminum retained in the sodium hydroxide precipitate by the small amounts of nickel present in most nitriding steels. The data obtained are given in Table 2. For these experiments faintly acid solutions (volume 150 ml) containing varying amounts of nickel, aluminum, and iron were poured slowly into 150 ml of a hot 10 per cent solution of sodium hydroxide (while stirring vigorously), boiled one minute and cooled. In experiments 1 to 6 the precipitate was filtered off and washed with a cold 1 per cent solution of sodium hydroxide. In experiments 1 to 3, aluminum was determined in the sodium hydroxide precipitate, after solution in acid, by double precipitation with ammonium hydroxide in the presence of considerable ammonium chloride. In experiments 4 to 6, aluminum was determined in the sodium hydroxide filtrates by double precipitation with ammonium hydroxide. In experiments 7 to 11, the solution, after precipitation with sodium hydroxide, was made up to 500 ml and aluminum determined in a filtered 250 ml aliquot portion by double precipitation with ammonium hydroxide. The aluminum thus found was multiplied by 2 to obtain, by difference, the total aluminum lost. Experiments 1 to 3 and 7 to 8 show that appreciable amounts of aluminum are carried down by the precipitate if moderate amounts of aluminum and nickel are treated with sodium hydroxide. However, experiments 4, 5, 9, and 10 show that the loss is negligible when nickel is precipitated in the presence of the amount of iron (approximately 0.2 g) usually retained in the bicarbonate precipitate. Experiment 6 shows that 0.350 g of chromium causes no significant retention of aluminum.

TABLE 2.—*Retention of aluminum by the sodium hydroxide precipitate*

Experiment No.	Al present	Other elements present	Al lost in NaOH precipitation	
			Single	Double
	g	*g*	*g*	*g*
1	0.0376	0.014 Ni	0.0025	0.0000
2	.0400	.044 Ni	.0062	.0025
3	.0100	.100 Ni	.0089	.0070
4	.0400	.014 Ni, .200 Fe	.0004	
5	.0400	.014 Ni, .200 Fe	.0004	
6	.0400	.350 Cr	.0003	
7	.0400	.014 Ni	.0022	
8	.0400	.040 Ni	.0058	
9	.0400	.040 Ni, .220 Fe	.0005	
10	.0400	.004 Ni, .050 Cr, .240 Fe	.0004	

In some procedures for the rapid determination of aluminum in steel, a faintly acid solution of all of the iron in a 2 to 5 g sample is slowly poured into an excess of sodium hydroxide, the solution diluted to a definite volume, and aluminum determined in a filtered aliquot portion. Such a procedure gives low results because some of the aluminum is retained by the very large precipitate of ferric hydroxide. For example, tests on a 3 g sample of a steel containing

1 per cent of aluminum showed an average loss corresponding to 0.06 per cent of aluminum. These tests were made by pouring the faintly acid solution (volume 250 ml) into 150 ml of a hot 12 per cent solution of sodium hydroxide, diluting to exactly 500 ml, determining aluminum in a filtered 300 ml portion by precipitating twice with ammonium hydroxide and correcting the ignited and weighed alumina for phosphorus, silica, and chromium. As would be expected, less aluminum is lost with steels of lower aluminum content. For example, tests on 2.5 g samples of steels containing 0.8 and 0.4 per cent of aluminum gave average losses corresponding to 0.05 and 0.03 per cent of aluminum, respectively. These errors are fairly constant, so that for rapid routine determinations on material of approximately constant composition a correction factor can be determined and applied. In such determinations, the bicarbonate separation is, of course, omitted, whereby the time required for an analysis (with final titration of the quinolate precipitate) is shortened to 1.5 to 2 hours.

3. PRECIPITATION OF ALUMINUM BY 8-HYDROXYQUINOLINE

In addition to aluminum, the sodium hydroxide filtrate will contain more or less of any molybdenum, vanadium, tin, arsenic, and phosphorus that may be present in the steels under test. Very small amounts of chromium, usually less than 0.5 mg, may also be present. Lundell and Knowles (8) have shown that aluminum can be precipitated with 8-hydroxyquinoline in the presence of molybdenum and vanadium by adding hydrogen peroxide to the solution prior to the addition of the quinoline reagent. By a combination of this method with Berg's (1) tartaric acid procedure aluminum can be separated from all of the elements that have been mentioned. This method of precipitation is described in Section III. The results obtained by titrating the aluminum quinolate thus precipitated in mixtures of known amounts of aluminum with various elements are shown by experiments 1 to 7 of Table 3.

TABLE 3.—*Results obtained in the determination of aluminum by titration of aluminum quinolate*

Experiment No.	Al present	Elements added	Al found	Difference
	g	*g*	*g*	*mg*
1	0.0099		0.0100	+0.1
2	.0200		.0201	+.1
3	.0200		[1].0202	+.2
4	.0260		.0259	−.1
5	.0200	0.010 Mo, .003 Cr	.0203	+.3
6	.0200	.010 Sn	.0201	+.1
7	.0199	.020 V	.0200	+.1
8	[2].0250		.0251	+.1
9	[3].0250	.01 Mo, .05 Cr, .004 Ni	.0251	+.1

[1] Dried at 135° C and weighed as aluminum quinolate.
[2] 0.05 g of Al plus 0.22 g of iron treated with NaOH as directed in Section III, the mixture diluted to 500 ml and aluminum determined in a filtered 250 ml portion by precipitation as quinolate and subsequent titration.
[3] Same as experiment 8, but 0.01 g Mo, 0.05 g Cr, and 0.004 g Ni were added before the sodium hydroxide precipitation.

III. RECOMMENDED PROCEDURE

Transfer 4 g of sample to a 500 ml Erlenmeyer flask, add exactly 50 ml of diluted sulphuric acid (1+9, accurately measured), cover with a watch glass, and heat gently. When action ceases, dilute to 150 ml with hot water, heat to boiling, and while agitating the solution add from a burette a solution containing 8.0 g of sodium bicarbonate per 100 ml of water until a permanent precipitate appears (approximately 38 ml in the usual case). At this point add 0.20 ml more for each miligram of aluminum anticipated. A 4 g sample of a steel containing 1.2 per cent of aluminum would require an excess of 9.6 ml of the bicarbonate solution. In no case, however, should less than 5 ml excess be added; that is, for steels containing less than 0.6 per cent of aluminum add a 5 ml excess of the bicarbonate solution. For high-chromium steels more bicarbonate will be needed. (See Section II.)

After adding the proper amount of bicarbonate solution, cover the flask, boil for one minute and let the precipitate settle. Filter immediately through a rapid 12.5 cm paper (No. 40 Whatman or equal) and wash the flask and precipitate twice with hot water. The filtrate will become cloudy in the funnel stem and receiving vessel owing to oxidation and hydrolysis of the iron, but this is of no consequence. Dissolve the bicarbonate precipitate by pouring 25 ml of hot diluted hydrochloric acid (1+2) drop by drop on it, and catch the solution in the original flask. Wash the paper and residue 8 to 10 times with hot diluted hydrochloric acid (1+19).[2] Add 1 ml of nitric acid (specific gravity 1.42) to the acid solution and washings, boil for two minutes and cool somewhat.

Nearly neutralize with a 30 per cent solution of sodium hydroxide, adjust the volume of the solution to 150 to 175 ml, warm to 70° C. and pour slowly into 150 ml of a hot 10 per cent solution of sodium hydroxide as the latter is vigorously stirred. Boil for one minute and cool the solution to room temperature. Transfer to a 500 ml volumetric flask and dilute to the mark. Pour into a dry 600 ml beaker. Stir well and let settle for about 30 minutes. Filter through a tight 12.5 cm paper (No. 42 Whatman or equal). Discard the first 25 to 35 ml portion and collect the next 250 ml in a 250 ml volumetric flask. Transfer the contents of the flask to a 600 ml beaker, washing the flask several times with water.

Neutralize the alkaline solution with hydrochloric acid (specific gravity 1.18), add an excess of 3 to 5 ml and 1 g of tartaric acid (5 ml of a 20 per cent solution). Add ammonium hydroxide (specific gravity 0.90) until the solution is just alkaline to litmus and then add 3 to 4 drops more. Add 10 to 15 ml of a fresh 3 per cent solution of hydrogen peroxide (or 1 to 1.5 ml of fresh perhydrol). Heat to 50° to 55° C. and add, dropwise and with constant stirring, a clear 2.5 per cent solution of 8-hydroxyquinoline [3] until 0.7 ml has been added for each milligram of aluminum anticipated, and then 5 ml more.

---

[2] Any aluminum which was present in the steel as Al_2O_3 will remain on the paper at this point. This can be included in the analysis, if the percentage of total aluminum is desired, by igniting the paper and residue, fusing with potassium pyrosulphate, dissolving the melt and adding to the main acid solution. This correction rarely exceeds 0.018 per cent of aluminum (equivalent to 0.035 Al_2O_3).

Since aluminum nitride is soluble in diluted hydrochloric acid (1+3), it is also probably soluble in diluted sulphuric acid (1+9), though this point was not checked.

[3] Prepared by triturating 2.5 g of 8-hydroxyquinoline with 5 ml of glacial acetic acid, pouring the resulting solution into 100 ml of water at 60° C., cooling and filtering.

For a steel containing 1.2 per cent of aluminum the volume needed would be $24 \times 0.7 = 16.8 + 5$, or 22 ml. Then add dropwise while stirring 2 ml of ammonium hydroxide (specific gravity 0.90) and stir with a mechanical stirrer for 12 to 15 minutes. Let settle for about 15 minutes, while cooling to room temperature, and filter by suction through a 50 cm fritted glass crucible of fine porosity such as a No. 4 Jena glass filtering crucible.[4] Wash the beaker and precipitate with about 60 ml diluted ammonium hydroxide (1+99) heated to about 50° C.

The precipitate can be either weighed or titrated.[5] In gravimetric determinations, dry the precipitate for 1.5 hours at 135° C. and weigh as $Al(C_9H_6ON)_3$ which contains 5.87 per cent of aluminum.

The titration procedure is equally accurate and is particularly suited for rapid work. If this procedure is to be used, place a clean flask under the funnel and pour 40 ml of hot (75° C.) diluted hydrochloric acid (1+6) on the washed precipitate. Let the reaction proceed for a few minutes and stir occasionally with a small glass rod before applying suction. As soon as the precipitate has dissolved apply suction, and wash the crucible first with about 75 ml of the hot diluted hydrochloric acid (75° C.) and then with 50 ml of water.

Dilute the acid solution to 250 ml, add 15 ml of hydrochloric acid, and cool to room temperature (21° C. ± 4°). The hydrochloric acid content of the solution during the subsequent bromination should not be less than 8 per cent.

Add a standard 0.35 *N* solution of potassium bromate-potassium bromide until in moderate excess (about 3 ml excess), as determined by test,[6] or by calculation if the approximate amount of aluminum is known. If the bromate solution is 0.35 *N* approximately 1.3 ml are required for each milligram of aluminum, and hence for a steel containing 1.2 per cent of aluminum there would be needed $24 \times 1.3 = 31.2 + 3$ ml excess, or 34 ml. Stir and let stand for 30 to 60 seconds to make sure that bromination is complete. Add 15 ml of a 25 per cent solution of potassium iodide, stir well to make sure that the reaction between bromine and iodide is complete, and then titrate with a standard solution of sodium thiosulphate until the color of the iodine becomes faintly yellow. At this point add 2 ml of starch solution and titrate to the disappearance of the blue color.

The following solutions are required for the titration method:

Potassium bromate-bromide solution (0.35 N).—Dissolve 9.743 g of potassium bromate and approximately 34 g of potassium bromide in 400 ml of water and dilute to exactly 1 liter. If pure bromate is used the theoretical titer for aluminum can be used. Usually it is more convenient to obtain the titer of the bromate by determining the ratio of the bromate solution to a thiosulphate solution which has been

[4] If fritted glass crucibles are not available the precipitate can be filtered through a tight paper, such as a Whatman No. 42. In this case the paper and precipitate should be washed about 10 times with 10 ml portions of cold diluted ammonium hydroxide (1+99).

[5] If a good grade of sodium hydroxide is used the blank will represent about +0.2 mg of aluminum. If it does not exceed this amount it can be neglected because it compensates for the small loss of aluminum that occurs in the sodium hydroxide precipitation. The blank on the alkali used was determined by precipitating 0.24 g of aluminum-free iron with sodium hydroxide, diluting to 500 ml filtering off a 250 ml portion, adding a definite amount of aluminum and then precipitating and titrating the aluminum quinolate. The difference between the aluminum value so obtained and that obtained by directly precipitating and titrating the same amount of aluminum represented the blank on the alkali.

[6] Made by adding a drop of the solution to a mixture of 1 drop of potassium iodide solution and 1 drop of starch solution on a spot plate. If the mixture turns blue, stir the test solution for one minute and again test. If the blue color does not again appear, more bromate solution must be added and the test repeated. Berg (1) uses a few drops of a 1 per cent aqueous solution of indigo-carmine. Hahn and Vieweg (3) use diazobenzene-sulphonic acid paper instead of iodide and starch.

standardized against a standard solution of 0.1 *N* permanganate. This ratio is obtained as follows: To 250 ml of water add 25 ml of the bromate solution, stir, add 25 ml of hydrochloric acid (specific gravity 1.19) and immediately add 15 ml of a 25 per cent solution of potassium iodide. Stir and titrate with the thiosulphate solution until the solution is nearly colorless. At this point add 2 ml of starch solution and titrate to the disappearance of the blue color. In titrating quinolates with potassium bromate 4 atoms of bromine are required for each quinolate radical. Consequently 12 atoms of bromine represent 1 atom of aluminum, and 1 ml of an exactly *N* solution of the bromate bromide would equal

$$\frac{26.97}{12}\times\frac{1}{1{,}000}=0.002248 \text{ g of aluminum}$$

The titer of the bromate solution is then obtained as follows:

$$\text{Normality factor of the thiosulphate solution}\times\frac{\text{ml of thiosulphate solution}}{\text{ml of bromate solution}}=\text{the normality factor of the bromate solution}$$

The latter $\times 0.002248$ = g of Al per ml of the bromate solution.

Sodium thiosulphate solution (0.35 N).—Dissolve 88 g of sodium thiosulphate ($Na_2S_2O_3\cdot 5H_2O$) in 300 ml of recently distilled water, add 0.1 g of sodium carbonate and dilute to one liter. Standardize by means of 0.1 *N* permanganate. (See (6) p. 118.)

Starch solution.—To 500 ml of boiling water add a cold suspension of 5 g of soluble starch in 25 ml of water. Cool, add a cool solution of 5 g of sodium hydroxide in 50 ml of water, then add 15 g of potassium iodide and mix thoroughly.

Potassium iodide solution (25 per cent).—Dissolve 25 g of potassium iodide in 100 ml of water.

The results that were obtained when this method was applied in the analysis of standard steel No. 106 are shown in Table 4. In addition to the data shown in the table, determinations of aluminum in synthetic mixtures designed to simulate a steel containing 0.5 per cent of aluminum, 1.25 per cent of chromium, and 0.2 per cent of molybdenum gave values of 0.49, 0.51, and 0.49.

TABLE 4.—*Results obtained by applying the recommended method in analysis of steel No. 106*

[Total Al=1.06 per cent, Al as Al_2O_3=0.017 per cent]

PERCENTAGE OF ALUMINUM OBTAINED	
By titration	By weighing precipitate after drying at 135° C
1.05	1.06
1.05	1.06
1.03	1.06
1.05	
1.06	[1] 1.08
1.05	
1.04	[1] 1.07
Average. 1.05	----------

[1] Includes recovery of aluminum in the residue from the acid treatment of the bicarbonate precipitate. The other values in this table do not include this recovery.

IV. BIBLIOGRAPHY

1. Berg, R., Z. anal. Chem., vol. 71, p. 375, 1927.
2. Britton, H. T. S., J. Chem. Soc., vol. 127, p. 2110, 1925.
3. Cunningham, T. R., Ind. Eng. Chem., Anal. ed., vol. 3, p. 103, 1931.
4. Hahn, F. L., and Vieweg, K., Z. anal. Chem., vol. 71, p. 122, 1927.
5. Hillebrand, W. F., and Lundell, G. E. F., "Applied Inorganic Analysis," p. 77, Wiley, 1929.
6. Lundell, G. E. F., Hoffman, J. I., and Bright, H. A., "Chemical Analysis of Iron and Steel," p. 74, Wiley, 1931.
7. Reference (6), p. 118.
8. Lundell, G. E. F., and Knowles, H. B., B. S. Jour. Research, vol. 3, p. 91, 1929, or Research Paper 86.
9. Swift, E. H., and Barton, R. C., J. Am. Chem. Soc., vol. 54, p. 4155, 1932.

WASHINGTON, December 15, 1932.

156547—33——4

THE OXIDATION OF ALPHA AND BETA GLUCOSE AND A STUDY OF THE ISOMERIC FORMS OF THE SUGAR IN SOLUTION [1]

By Horace S. Isbell and Ward Pigman

ABSTRACT

The method of bromine oxidation in the presence of barium carbonate has been applied to the measurement of the rates at which the various forms of *d*-glucose react with bromine water. Under the conditions described *β*-*d*-glucose is oxidized about thirty-five times as fast as *α*-*d*-glucose. The delta lactone of gluconic acid is the predominating product in both cases, and it is formed without the intermediate production of gluconic acid. This indicates that *α*- and *β*-*d*-glucose contain the 1, 5 or amylene oxide ring. The oxidation of an equilibrium solution of *d*-glucose progresses rapidly, until all of the beta glucose present in the solution is used up, and then more slowly as the oxidation of the alpha form is continued. The rate of oxidation indicates that the equilibrium solution contains about 64 per cent beta and 36 per cent alpha glucose. There can be little doubt but that the equilibrium of glucose is more complex than the simple equilibrium between the alpha and beta forms, but the absence of substantial amounts of the free acid and the gamma lactone in the product of oxidation is evidence that the equilibrium solution of the sugar does not contain large proportions of the free aldehyde and of the gamma form. It is believed that the application of the methods of investigation described in this report will yield much useful information as to the composition of sugar solutions and the changes which occur during the mutarotation reaction.

CONTENTS

	Page
I. Introduction	337
II. Oxidation of alpha and beta glucose	338
III. Reaction rates	344
IV. Experimental details	352
1. Oxidation of *β*-*d*-glucose to gluconic delta lactone	352
2. Oxidation of *α*-*d*-glucose to gluconic delta lactone	354
3. Measurement of reaction rates	355
4. Mutarotation of *α*-*d*-glucose at 0° C	356
V. Applications of method	356

I. INTRODUCTION

Inasmuch as solutions of reducing sugars presumably contain a number of isomeric forms of the sugar in equilibrium, it is desirable to ascertain which isomer is the active reductant in any oxidation. Previous investigators have assumed that solutions of the aldoses contain small quantities of the aldehyde form of the sugars and that the monocarboxylic acid is derived by the oxidation of this free aldehyde. It was shown by Isbell and Hudson [2] that the optical rotation of a buffered glucose solution, upon bromine oxidation, rises to a point which corresponds with the rotation of the delta lactone, and then the rotation decreases to a minimum value at a rate approximately

[1] This paper was presented at the meeting of the American Chemical Society, New Orleans, La., March 29, 1932.

[2] Isbell and Hudson, B. S. Jour. Research, vol. 8 (RP418), p. 327, 1932.

the same as the hydrolysis of the delta lactone to the corresponding acid. Subsequently it was shown by Isbell [3] that the free acid is not formed in the course of the oxidation of the aldoses with bromine water by conducting the reaction in the presence of barium carbonate. The latter neutralizes the free acid but does not react with the lactone, thereby differentiating between the two substances. This method, as well as the changes in optical rotation and acidity, prove that delta lactones are obtained prior to the acids from α- and β-*d*-mannose, α- and β-*l*-rhamnose, α- and β-lactose, and β-maltose. Therefore, it is apparent that the normal aldoses, at least in slightly acid solution, do not yield acids by bromine oxidation and consequently there is no foundation for the heretofore accepted concept that the reaction takes place through the straight-chain aldehyde form of the sugar. Since, in strongly acid solutions, the oxidations are slow and the oxidation products are rapidly converted into equilibrium mixtures containing the free acid, the delta and gamma lactones, extreme care must be exercised in the interpretation of the results thus obtained.

In a paper entitled "A Possible Source of Error in Determining the Constitution of Di and Polysaccharides," published prior to the publication of Isbell and Hudson,[4] on "The Course of the Oxidation of the Aldose Sugars with Bromine Water," but subsequent to the actual work done by Isbell and Hudson, Irvine and McGlynn [5] make the following statement: "Crystalline 2, 3, 6 trimethyl glucose if oxidized with bromine water under conditions which permit the accumulation of hydrogen bromide yields directly the gamma lactone of 2, 3, 6 trimethyl gluconic acid as the main product—but when the sugar is oxidized by the same reagent in the absence of halogen acid, the delta lactone is produced in preponderating amount." However, as pointed out by Hirst,[6] their experimental work does not show that the gamma lactone is formed directly because the reaction in acid solution was allowed to continue eight hours, which is ample time, especially in the presence of hydrobromic acid, for the primary oxidation product to be rearranged into the gamma lactone. Irvine and McGlynn's experimental procedure, also, did not show that the delta lactone was the primary oxidation product of the bromine oxidation in the absence of halogen acid, because they allowed the reaction to proceed for eight hours in the presence of calcium carbonate. In eight hours the lactone would have been hydrolyzed, for the most part, to give the free acid, which would have reacted in turn with calcium carbonate to give the calcium salt. Irvine and McGlynn state: "The calcium salts in solution were decomposed by the addition of the required amount of oxalic acid, the product extracted with chloroform and isolated in the usual manner." By this procedure a mixture containing the delta and gamma lactones would have been obtained regardless of the nature of the initial oxidation product.

II. OXIDATION OF ALPHA AND BETA GLUCOSE

The method, which has been reported in previous publications,[7] consists in oxidizing the sugar with bromine water in a solution saturated with carbon dioxide and buffered with a suspension of barium

[3] Isbell, B. S. Jour. Research, vol. 8 (RP441), p. 615, 1932.
[4] See footnote 2, p. 337.
[5] Irvine and McGlynn, J. Am. Chem. Soc., vol. 54, p. 359, 1932.
[6] Hirst, J. Am. Chem. Soc., vol. 54, p. 2559, 1932.
[7] Isbell, see footnote 3, p. 338; also J. Am. Chem. Soc., vol. 54, p. 1692, 1932.

carbonate. The barium carbonate prevents the solution from becoming strongly acid, and consequently the oxidation is rapid, while the mutarotation reaction is slow. In the present instance the crystalline sugar or the equilibrium mixture was added to the buffered bromine solution and from time to time the oxidation was stopped by removing the bromine through reaction with an unsaturated oil or hydrocarbon; the excess buffer (barium carbonate) was then separated by filtration, leaving a solution containing the oxidation product, any unoxidized sugar, barium bromide, and traces of barium bicarbonate. Any free gluconic acid, formed either in the course of the oxidation or by the hydrolysis of the lactone, would be neutralized by the barium carbonate giving barium gluconate, while the unchanged lactone would exist in the solution as such. The amount of the lactone in the solution was determined by titration; the unoxidized sugar was determined by reduction of Benedict's solution; and the amount of gluconic acid neutralized by the barium carbonate was estimated by difference. Portions of the solutions containing the oxidation products were used also for measuring the optical rotations and the hydrogen-ion concentrations. The results obtained from α and β-*d* glucose and the equilibrium solution are given in Tables 1 and 2.

TABLE 1.—*Comparison of the oxidation products with the delta lactone*

α-d-glucose, oxidation 85.5 per cent complete in 20 minutes			β-d-glucose, oxidation 97.5 per cent complete in 3 minutes			d-glucose in equilibrium, oxidation 77.2 per cent complete in 5 minutes			Gluconic delta lactone		
	$[\alpha]_D^{20}$	*pH*[1]		$[\alpha]_D^{20}$	*pH*		$[\alpha]_D^{20}$	*pH*		$[\alpha]_D^{20}$	*pH*
Minutes			*Minutes*			*Minutes*			*Minutes*		
26	50.6	5.1	13	62.4	4.8	14	65.8	4.9	13	61.7	4.6
30	49.7	4.5	15	61.9	4.5	15	65.6	4.7	15	61.4	4.3
40	47.8	3.9	25	60.1	3.6	30	61.5	3.7	25	59.9	3.5
90	39.8	3.3	40	57.3	3.2	45	58.0	3.6	40	57.1	3.1
210	26.8	3.0	60	52.0	2.9	73	52.4	3.3	60	53.8	2.8
355	18.0	2.9	150	27.8	2.5	133	42.3	3.0	150	32.0	2.4
Hours			*Hours*			*Hours*			*Hours*		
24	12.0	-------	305	10.1	2.5	338	24.1	2.7	315	14.6	2.4
			Hours			*Hours*			*Hours*		
-------	-------	-------	24	7.1	-------	22	19.4	-------	24	7.5	------

[1] Measurements made at 25° C. in solutions containing CO_2 and $BaBr_2$.

TABLE 2.—*Saponification of the oxidation products in solutions buffered with $BaCO_3$ and CO_2 at 25° C.*[1]

Product from α-d-glucose		Product from β-d-glucose		Product from equilibrium solution of d-glucose		Gluconic delta lactone	
Time	Per cent of product not saponified	Time	Per cent of product not saponified	Time	Per cent of product not saponified	Time	Per cent of product not saponified
Minutes		*Minutes*		*Minutes*		*Minutes*	
25	87.4	7	95.8	9	87.1	7.5	93.6
85	63.0	65	70.8	67	63.3	95	62.8
205	40.2	186	43.7	181	36.9	186	44.8
326	29.5	300	26.3	318	21.5	300	20.65
1,440	10.7	1,440	0.7	1,440	2.85	1,440	00

[1] The measurements were made with portions of the solutions given in Table 1.

The sample of β-*d*-glucose was oxidized to the extent of 97.5 per cent in 3 minutes at 25° C., and 7 minutes after the beginning of the oxidation 95.8 per cent of the product existed in the solution as unchanged lactone. Inasmuch as a sample of the delta lactone did not give a higher percentage of unchanged lactone after shaking 7 minutes with barium carbonate, the small fraction (4.2 per cent) of the oxidation product which was apparently neutralized by the barium carbonate probably resulted from the acid set free by hydrolysis. Hence there is very little, if any, free gluconic acid formed by the bromine oxidation of β-*d*-glucose in the presence of barium carbonate. The solution containing the lactone or oxidation product from β-*d*-glucose gave $[\alpha]_D^{20} = +62.4°$, 13 minutes after the addition of the bromine, and in 24 hours the specific rotation decreased to a minimum value of +7.1 and then slowly increased. The delta lactone of gluconic acid under similar conditions gave $[\alpha]_D^{20} = +61.7°$, 13 minutes after solution, decreasing in 24 hours to a minimum of +7.5 and thereafter slowly increasing in value. These results are in qualitative agreement with the work of Nef [8] on the delta lactone, who also reported that the gamma lactone, on the other hand, gives $[\alpha]_D^{20} = +67.82$ initially, which decreases in 24 hours to $[\alpha]_D^{20} = +61.3$.

The changes in the hydrogen-ion concentration (pH) of the products obtained from α- and β-*d*-glucose, as well as the equilibrium solution, show that the products obtained after removing the barium carbonate develop acidity on standing in aqueous solution. The changes in acidity on standing are similar to those observed for the delta lactone of gluconic acid under like conditions.

The rates of saponification given in Table 2 were determined by titration after shaking the samples with a suspension of barium carbonate in water, saturated with carbon dioxide. The curves in Figure 1 were obtained by plotting the data on a semilogarithmic scale. The amount of unchanged lactone is expressed as the logarithm of that fraction of the product, originally added or theoretically formed by oxidation, which remains at any given time. Since the slopes of the curves are nearly the same the various products are saponified at approximately equal rates.

From Table 2 it can be seen that after 186 minutes, 43.7 per cent of the oxidation product from β-*d*-glucose had not reacted with barium carbonate and that under like conditions gluconic delta lactone was unchanged to the extent of 44.8 per cent. After 24 hours no unchanged gluconic delta lactone remained in the solution, while under like conditions 0.7 per cent of the oxidation product derived from β-*d*-glucose remained in a form capable of neutralizing an alkali.

The oxidation of α-*d*-glucose probably takes place in much the same manner as the oxidation of β-*d*-glucose, but since the alpha form is oxidized more slowly than the beta form, the measurement of the properties of the oxidation product derived from α-*d*-glucose is complicated by the presence of unoxidized sugar and by side reactions which may occur during the relatively long time required for the reaction. The changes in rotation, hydrogen-ion concentration, and the rates of saponification show qualitatively that the delta lactone is the principal product derived by the oxidation of α-*d*-glucose with bromine water in the presence of barium carbonate. But as shown

[8] Nef, Ann., vol. 403, p. 324, 1914.

in Table 2, 10.7 per cent of the oxidation product derived from alpha glucose and 2.8 per cent of the product derived from the equilibrium solution were not saponified in 24 hours (1,440 minutes). This relatively inert material may arise from some form of the sugar which is produced during the mutarotation reaction. The oxidation of the alpha sugar required a longer time and consequently there was more opportunity for the oxidation of substances which might be formed in the course of the mutarotation reaction. However, the oxidation of a solution of *d*-glucose in equilibrium does not reveal the presence of a large quantity of products other than the delta lactone. The oxidation of the equilibrium solution of *d*-glucose, comparable to the oxidations of alpha and beta sugars which have been given, was 77.2 per cent complete in 5 minutes, and 4 minutes later 87.1 per cent of the

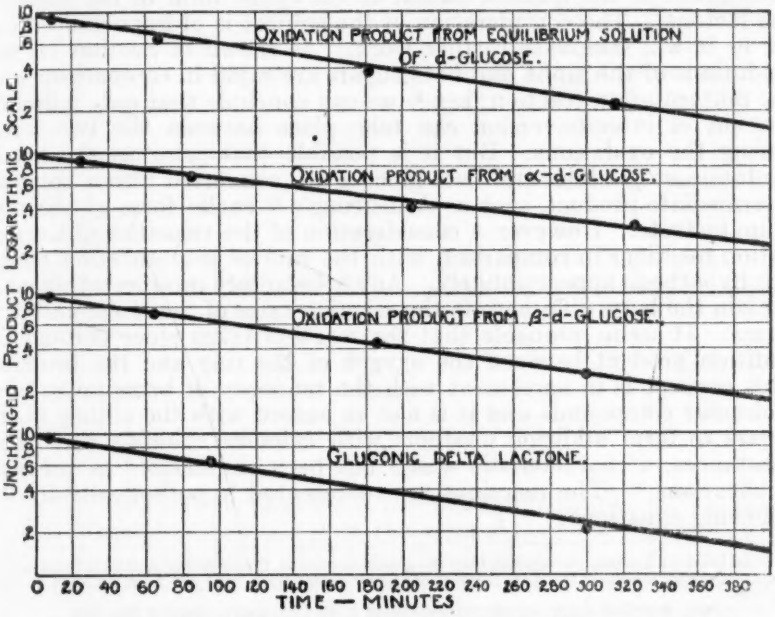

OXIDATION PRODUCT FROM EQUILIBRIUM SOLUTION OF d-GLUCOSE.
OXIDATION PRODUCT FROM α-d-GLUCOSE.
OXIDATION PRODUCT FROM β-d-GLUCOSE.
GLUCONIC DELTA LACTONE.
UNCHANGED PRODUCT LOGARITHMIC SCALE.
TIME — MINUTES
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380

FIGURE 1.—*Saponification in solutions buffered with $BaCO_3$ and CO_2*

reaction product remained in the solution as unchanged lactone. As noted above, this unchanged lactone contains a small amount of some substance which is saponified more slowly than the delta lactone. Inasmuch as this substance may give valuable information in regard to intermediate products of the mutarotation reaction, it is being investigated further in order to ascertain what it is and to determine the conditions which give rise to its formation.

As a final step in the proof for the formation of the delta lactone by oxidation of β-*d*-glucose, the crystalline delta lactone was separated from the reaction mixture. The oxidation was conducted in the same manner as before, but the product, which contained very little unoxidized sugar, was extracted with a solvent (dioxane) which dissolves the lactone, but does not dissolve the inorganic salts. The solution of the oxidation product, on evaporation at a low temperature in

vacuo, readily gave the crystalline delta lactone.[9] In some cases the delta lactone was separated within one-half hour after the addition of the sugar to the bromine water, the experimental conditions being such that an alteration in the oxidation product was unlikely.

The physical and chemical measurements, which have been given, prove that the delta lactone is the predominating product of the reaction in each case and that it does not originate from gluconic acid by spontaneous lactone formation. It is emphasized that the measurements were made during the course of the oxidation and immediately thereafter, thereby confirming the previously advanced hypothesis of Isbell and Hudson that the cyclic forms of the normal sugars give delta lactones by oxidation with bromine water.

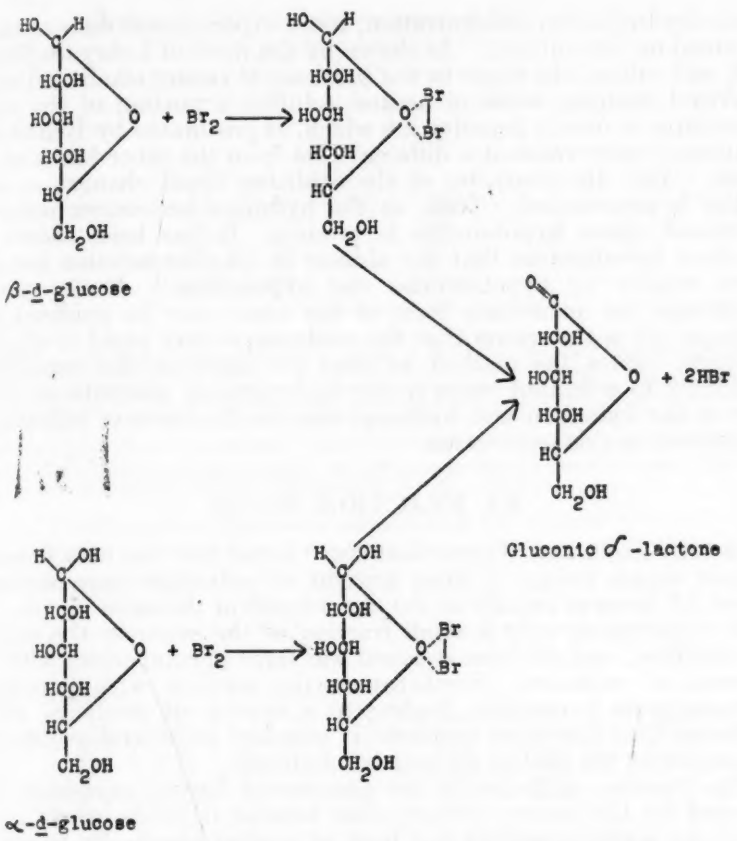
At this time there is no direct experimental evidence as to the exact mechanism of the transformation of the cyclic form of the sugar to the lactone. The consideration of the subject is of importance in so far as it will stimulate further work. As shown in Section III the oxidations of the alpha and beta sugars are rapid in comparison with the mutarotation reaction; hence we can conclude that only a limited amount of interconversion can take place between the two forms during the oxidations. But it is possible that prior to the actual oxidation step, alpha and beta glucose are converted into a common intermediate product, such as Armstrong's [10] enolic form of the oxonium hydrate. However, a consideration of the velocities of the oxidation reactions in comparison with the rate of mutarotation makes this hypothesis appear unlikely. Any satisfactory interpretation must explain the large difference in the reaction rates of the alpha and beta forms. It seems probable that the reaction takes place through an addition product between the oxygen of the ring and the bromine. This concept is in agreement with the tendency of bromine to form molecular compounds and it is also in accord with the ability of the sugars to form addition products with calcium chloride and other substances, a characteristic which has been emphasized in previous publications.[11] The reactions are represented hypothetically by the following equations:

---

[9] Since the delta lactones are obtained from the aldoses in general, the oxidation method is being applied to the preparation of some of the delta lactones of aldonic acids which have not been obtained by other methods.

[10] Armstrong, The Carbohydrates and the Glucosides, p. 47, Longman's, Green & Co., 1924.

[11] Isbell, B. S. Jour. Research, vol. 5 (RP226), p. 741, 1930; vol. 7 (RP396), p. 1, 1931.



If a bromine addition product is formed as illustrated above, when the hydrogen of carbon one is on the same side of the ring and in the vicinity of the bromine it will be in a favorable position for oxidation. When the hydrogen is on the opposite side of the ring it will be in a less favorable position for oxidation and, since the hydrogen of the hydroxyl group, which is now in proximity to the bromine, is already in an oxidized state, the reaction will proceed more slowly. In models of α- and β-d-glucose with the hydrogen and hydroxyls on the first carbon allocated according to the work of Boëseken [12] the hydrogen on the first carbon lies on the same side of the ring as the oxygen in beta glucose and on the opposite side in alpha glucose. Hence the hydrogen is in a favorable position for oxidation in the beta form and in a less favorable position in the alpha. The spacial relations may be best understood by recourse to the conventional 3-dimensional models of alpha and beta glucose which can be conveniently made by means of tetrahedrons such as those described by Brauns.[13]

Inasmuch as there are several interpretations which may be advanced to account for the changes in the reaction rates with changes

[12] Boëseken, Ber., vol. 46, p. 2612, 1913.
[13] Brauns, D. H., J. Am. Chem. Soc., vol. 51, p. 1824, 1929.

in the hydrogen-ion concentration, more experimental data must be obtained on this subject. As shown by the work of Lobry de Bruyn, Nef, and others, the sugar in the presence of strong alkali undergoes profound changes, while in neutral solution a portion of the sugar dissociates to form a negative ion which, as postulated by Bunzel and Mathews,[14] may react at a different rate from the other forms of the sugar. Also, the character of the oxidizing agent changes as neutrality is approached. Thus, as the hydrogen-ion concentration is decreased, more hypobromite is present. It has been shown by previous investigators that the aldoses in alkaline solution are oxidized rapidly by hypobromites and hypoiodites.[15] Under certain conditions the open-chain form of the sugar may be oxidized and perhaps this is the reason that the oxidation is very rapid in alkaline solution. Since the method as used for studying the reaction is restricted to a limited range in the hydrogen-ion concentration, the rôle of the hydrogen and hydroxyl ions in the reaction will not be considered in this publication.

III. REACTION RATES

In 1925 Kuhn and Wagner-Jauregg [16] found that the beta forms of certain sugars reduce a given amount of potassium permanganate about 1.7 times as rapidly as the alpha forms of the same sugars. In their experiments only a small fraction of the sugar in the sample was oxidized, and the time required was large in comparison with the amount of oxidation. Furthermore, the reaction with potassium permanganate is complex, leading to a number of products, which indicates that the sugar molecule is attacked at several points and consequently the results are largely empirical.

The bromine oxidation in the presence of barium carbonate was selected for the present investigation because it yields nearly quantitatively a single product and may be studied kinetically to obtain valuable information as to the substances involved in the reaction. Particular attention was directed to maintaining conditions such that there was very little alteration in the sugar prior to oxidation. The experimental method was essentially as outlined on page 339 except that the temperature was maintained at 0° C. and samples were taken at more frequent intervals. Under these conditions, as previously noted by Isbell,[17] the beta sugars are oxidized much more rapidly than the alpha sugars. Our results show that beta glucose is oxidized about 35 times as rapidly as alpha glucose, a much larger difference than found by the method of Kuhn and Wagner-Jauregg.

[14] Bunzel and Mathews, J. Am. Chem. Soc., vol. 31, p. 464, 1909.
[15] Romijn, Z., Anal. Chem., vol. 36, p. 349, 1897; also Goebel, J. Biol. Chem., vol. 72, p. 802, 1927.
[16] Kuhn and Wagner-Jauregg, Ber., vol. 58, p. 1441, 1925.
[17] See footnote 3, p. 338.

TABLE 3.—*Oxidation of β-d-glucose*[1] *at 0.3° C.* ± *0.3°*

Time	Unoxidized sugar	Oxidized sugar	ak_β [2]	k_β
1	2	3	4	5
Minutes	*g*	*Per cent*		
1.3	3.495	22.4		
3.3	2.330	48.2	0.0878	
5.1	1.655	63.2	.0853	
8.3	.837	81.4	.0886	
11.1	.483	89.3	.0878	
15.5	.204	95.5	.0871	
25.3	.080	98.2	(.0681)	
		Average.	.0873	1.26

[1] Crystalline β-d-glucose (4.5 g) was added to a mixture of 500 ml of aqueous barium bromide, 10 ml of bromine, and 30 g of barium carbonate. The barium bromide solution contained 30 g of $BaBr_2 \cdot 2H_2O$ and was saturated with CO_2. The average of the bromine determinations by $Na_2S_2O_3$ titrations was 0.351 moles per liter and the average bromide content (calculated as given on p. 355) was 0.412 moles per liter. The concentration of free bromine as determined from equation (8), p. 348, was 0.0692 moles Br_2 per liter.

[2] $ak_\beta = \frac{1}{t} \log \frac{A}{A-x}$, where A is the amount of sugar (77.6 per cent) at the time of the first observation, and x is the amount of oxidation during the time, t, which is measured from the first observation. The concentration of the oxidant (free bromine) is represented by a. (See p. 346.)

TABLE 4.—*Oxidation of α-d-glucose at 0.3° C.* ± *0.3°* [1]

Time	Unoxidized sugar	Oxidized sugar	Bromine by $Na_2S_2O_3$ titration	k_1+ak_α [2]	ak_α	k_α
1	2	3	4	5	6	7
Minutes	*g*	*Per cent*	*Moles per l*			
1.4	4.59	0	0.363			
5.1	4.47	2.6	.372	(0.00313)	(0.00261)	
30.0	3.83	16.6	.374	.00276	.00224	
60.1	3.27	28.8	.378	.00252	.00200	
120.0	2.335	49.1	.374	.00247	.00195	
180.2	1.640	64.3	.371	.00250	.00198	
240.0	1.190	74.1	.367	.00246	.00194	
300.2	0.565	87.7	.396	(.00305)	(.00253)	
Average			.374	.00254	.00202	0.0238

[1] The sample of α-d-glucose was treated like the sample of beta glucose given in footnote 1, Table 3. The average bromide content (calculated as given on p. 355) was 0.381 moles per liter, and the average concentration of free bromine as calculated by equation (8), p. 348, was 0.085 moles of Br_2 per liter.

[2] $k_1+ak_\alpha = \frac{1}{t} \log \frac{A}{A-x}$, where A is the amount of sugar at the beginning of the time interval, t, and x is the amount of oxidation. The value k_1 is assigned a value of 0.00052. (See p. 349.)

TABLE 5.—*Oxidation of d-glucose equilibrium solution at 0.5° C.* ± *0.3°* [1]

Time	Unoxidized sugar	Oxidized sugar	Bromine by $Na_2S_2O_3$ titration
1	2	3	4
Minutes	*g*	*Per cent*	*Moles per l*
1.3	3.90	13.4	0.346
4.8	2.74	39.1	.340
9.7	1.99	55.8	.338
15.0	1.76	60.9	.336
30.2	1.56	65.3	.336
122.4	1.055	76.6	.329
239.9	.710	84.2	.322
329.9	.560	87.6	.312

[1] An equilibrium solution of d-glucose containing 4.5 g of sugar was added to a solution of bromine in aqueous barium bromide which gave a mixture similar to that described in footnote 1, Table 3. The average of the bromine determinations by $Na_2S_2O_3$ titration was 0.332 moles per liter, the average bromide content was 0.412 moles per liter, and the average concentration of free bromine was 0.063 moles per liter.

As shown in Figure 2, the oxidation of the sample of beta glucose was 50 per cent complete in about 3 minutes, while under like conditions the alpha form required about 130 minutes. The oxidation of the equilibrium solution progressed rapidly until the beta sugar was used up and then more slowly as the alpha form continued to be oxidized. This marked change in the reaction rate, during the oxidation of the equilibrium solution, has not been noted by previous investigators. As will be shown in subsequent publications, the study of the reaction rates affords means for ascertaining the proportions of the alpha and beta forms of the sugar in aqueous solutions and for deriving information concerning the equilibria existing in such solutions.

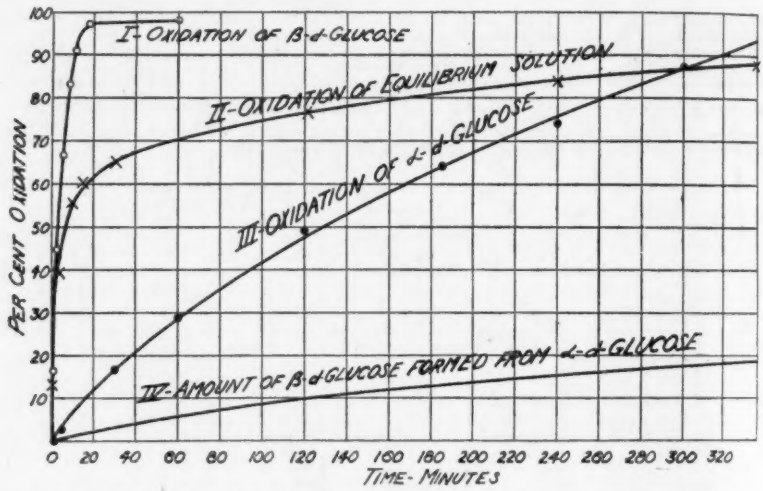


FIGURE 2.—*Bromine oxidation of d-glucose in the presence of* $BaCO_3$

To simplify conditions, by making the reaction practically a monomolecular one, a large excess of bromine was used. Under such conditions the velocity constant for the reaction may be calculated by means of the formula:

$$ak_\beta = \frac{1}{t} \log \frac{A}{A-x}$$

where A is the amount of sugar at zero time, x is the quantity of sugar which has been oxidized during the time interval, t, and a is the concentration of the oxidant.

The data for the experiment on β-*d*-glucose, which is illustrated in Figure 2, are given in Table 3. The fairly uniform values of ak_β, given in column 4, show that the reaction proceeded at a uniform rate. This is evidence that the sample does not contain two forms of the sugar which are oxidized at different rates. That is, β-*d*-glucose $[\alpha]_D^{20} = +19°$, is a homogeneous substance and not a mixture containing two isomers, such as the molecular compounds of lactose reported by Hockett and Hudson.[18]

[18] Hockett and Hudson, J. Am. Chem. Soc., vol. 53, p. 4455, 1931.

Since in the experiment under discussion the concentration of the oxidant was maintained practically constant, the effect of varying the concentration of bromine will now be considered.

Previously Bunzel and Mathews [19] studied the rate of the oxidation of equilibrium solutions of *d*-glucose with bromine water. They found that the reaction was retarded by the presence of small quantities of acid and that at a given hydrogen-ion concentration the rate of the reaction depended on the concentration of the sugar and the free bromine. They used a large excess of sugar and measured the rate at which the bromine decreased in the solution. Inasmuch as only a fraction of the total sugar was oxidized, their results do not reveal the changes in the reaction rates reported in this paper. It is necessary to study the oxidation of the alpha and beta forms of the sugars separately in order to determine the true characteristics of the individual reactions. In the present investigation, measurements of the reaction rates of α and β-*d*-glucose using different concentrations of bromine and barium bromide were made in order to determine whether the total bromine, free bromine, or hypobromous acid is the active oxidant. Since we were unable to find any data relating to the concentration of free bromine in barium bromide solutions, for our calculations, we used formulas derived by Jones and Hartmann [20] for bromine-potassium bromide solutions. The concentrations of free bromine and hypobromous acid thus obtained are only approximate and are applied to the problem at hand with that understanding. Jones and Hartmann assigned the following equilibrium constants to the reaction under consideration:

$$Br_2 + H_2O \rightleftarrows HBrO + \overline{Br} + \overset{+}{H}$$

$$K_H = \frac{(\overset{+}{H})(\overline{Br})(HBrO)}{(Br_2)} = 5.7 \times 10^{-10} \qquad (1)$$

$$Br_2 + \overline{Br} \rightleftarrows \overline{Br_3}$$

$$K_3 = \frac{(Br)(Br_2)}{(\overline{Br_3})} = 0.051 \qquad (2)$$

$$2Br_2 + \overline{Br} \rightleftarrows \overline{Br_5}$$

$$K_5 = \frac{(\overline{Br})(Br_2)^2}{(\overline{Br_5})} = 0.0246 \qquad (3)$$

$$B = \overline{Br} + \overline{Br_3} + \overline{Br_5} \qquad (4)$$

$$C = Br_2 + \overline{Br_3} + 2\overline{Br_5} + (HBrO) \qquad (5)$$

The symbols represent the concentrations of the various ions and molecules in the equilibrium solution. The concentrations of the free bromine (Br_2) and the hypobromous acid (HBrO) are obtained by solving Jones and Hartmann's equations simultaneously and substituting the experimental values for the total bromine (C), total bromide (B), and hydrogen-ion concentration ($\overset{+}{H}$). As the concentration of HBrO is extremely small, it was neglected in equation (5). Equation (6) is obtained by substituting in equation (4) the value of $\overline{Br_3}$ derived

[19] Bunzel and Mathews, J. Am. Chem. Soc., vol. 31, p. 464, 1909; also Bunzel, J. Biol. Chem., vol. 7, p. 157, 1910.

[20] Jones and Hartman, Trans. Am. Electrochem. Soc., vol. 30, p. 295, 1916.

from equation (2) and the value of $\overline{Br_5}$ derived from equation (3) and then solving for $\overline{Br}$.

$$\overline{Br}=\frac{B}{1+\frac{Br_2}{0.051}+\frac{Br_2^2}{0.0246}} \tag{6}$$

Equation (7) is obtained by eliminating $\overline{Br_5}$ between equations (4) and (5).

$$2B-C=2\overline{Br}-Br_2+\overline{Br_3} \tag{7}$$

By substituting in equation (7) values of $\overline{Br_3}$ and $\overline{Br}$ in terms of Br_2 as derived from equations (2) and (6), respectively, and simplifying, equation (8) is obtained. This equation was used for determing the concentration of free bromine.

$$Br_2^3+(0.482+2B-C)Br_2^2+[0.0246+0.482(B-C)]Br_2 -0.0246C=O \tag{8}$$

Since the value of Br_2 is small the equation was solved easily by the method of successive approximations. In a preliminary calculation Br_2^3 was neglected and an approximate value of Br_2 was obtained. The cube of the value thus obtained was then substitued in equation (8) and the resulting quadratic equation solved again for Br_2. After repeating this process several times the numerical value of Br_2 approached a constant which is the correct root of the equation.

The concentration of HBrO was calculated from the free bromine (Br_2), total bromide (B), and bromine (C) by means of equation (9) which was derived by substituting in equation (7) the value of $\overline{Br_3}$ from equation (2) and the value of $\overline{Br}$ in terms of $\overset{+}{H}$, HBrO, and Br_2 obtained from equation (1). The numerical value of $\overset{+}{H}$ is 4×10^{-6}.

$$HBrO=\frac{28\times10^{-4}(0.102+Br_2)(Br_2)}{2B-C+Br_2} \tag{9}$$

TABLE 6.—*Correlation of rate of oxidation of β-d-glucose with concentration of free bromine* [1]

Experiment No.	β-d-glucose	B [2] (Bromide)	C [3] (Bromine)	Free bromine (calculated)	HBrO (calculated)	Oxidation after—			ak_β	k_β
						5 minutes	10 minutes	15 minutes		
	1	2	3	4	5	6			7	8
	Moles per l	*Equivalents per l*	*Moles per l*	*Moles per l*	*Moles per l* $\times10^{-4}$	*Per cent*	*Per cent*	*Per cent*		
1	0.0496	0.412	0.351	0.0692	0.612	62.5	86.7	95.0	0.0873	1.26
2	.0496	.238	.179	.0477	.580	56.7	80.9	91.0	.0714	1.50
3	.0496	.564	.186	.0196	.069	26.1	47.4	61.5	.0272	1.39
4	.0496	.564	.182	.0192	.068	26.8	47.0	60.5	.0272	1.42
5	.0496	.560	.176	.0182	.064	24.7	44.2	59.3	.0253	1.39
Average										1.39

[1] The results for each experiment were derived from an experiment similar to that given in Table 3. The temperatures were 0.5° C. ±0.3°, except for experiment 1, which was 0.3° C.±0.3°. The calculations are based on that data given in this table except for experiment 1 which gives the averages reported in Table 3.

[2] Average bromide content, which corresponds to B in equation (4), p. 347.

[3] Average bromine by $Na_2S_2O_3$ titration, which corresponds to C in equation (5), p. 347.

The experiments tabulated in Table 6 were conducted to give information concerning the active oxidant. The first experiment is the one illustrated in Figure 2, curve 1, and given in detail in Table 3, while the others differ in the amounts of bromine and barium bromide employed. In experiments 2 and 5 approximately equal amounts of bromine were used, yet the values obtained for ak_β (column 7) were 0.0714 and 0.0253, which clearly shows that the reaction rate is not determined by the total quantity of bromine. It is also apparent that hypobromous acid is not the oxidant since a tenfold variation in the HBrO was accompanied by only a threefold change in reaction rate. The values for k_β, reported in column 8, based on the assumption that free bromine is the active oxidant, differ slightly among themselves, but they are sufficiently constant to indicate that free bromine is the oxidant. The variations are due in part to small unavoidable differences in temperature. In addition, it will be recalled that the data used for estimating the concentration of free bromine were assumed to be the same as those found by Jones and Hartmann for relatively dilute bromine-potassium bromide solutions and hence the differences in the constants may be partially ascribed to inadequate knowledge as to the concentration of the free bromine in the specific solutions used in these experiments.

Since the oxidation of *α-d*-glucose is relatively slow, allowance must be made for the stereoisomeric conversion of the alpha to the beta form while the oxidation is taking place. The resulting beta sugar would be oxidized nearly as rapidly as it is formed. Hence, we can consider the oxidation as consisting of two reactions, namely, the oxidation of the alpha form directly, and the conversion of the alpha to the beta form with the subsequent rapid oxidation thereof. In the event that a constant amount of the oxidant is maintained, we can assume as an approximation that we are dealing with only two simultaneous first-order reactions and apply the customary formula to obtain the velocity constants: $k+k_1=\frac{1}{t}\log\frac{A}{A-x}$. In this formula, k represents the velocity constant for the oxidation of the alpha form directly; k_1 represents the velocity constant for the conversion of the alpha form to the beta with the subsequent oxidation of the same. Inasmuch as the oxidation of the beta sugar is rapid, it can be assumed that the value of k_1 is determined by the rate at which the beta sugar is formed by the mutarotation reaction.

This was calculated from mutarotation data, determined under conditions similar to those used in the oxidation experiments. The value thus obtained, 0.00052, is approximately 20 per cent of the value of the constant representing the sum total of the reaction given in column 5 of Table 4. In other words, the sugar is oxidized about five times as fast as the alpha form of the sugar is converted to the beta form. The amount of alpha glucose converted to beta glucose while the reaction is taking place, is represented in Figure 2, page 346, by curve 4. Since the beta sugar is oxidized nearly as rapidly as it is formed, the distance from the base line to the lower curve represents approximately the amount of alpha glucose which is converted to beta glucose and then oxidized, while the vertical distance from curve 4 to curve 3 represents the maximum amount of alpha glucose oxidized as such. The amount of beta glucose converted to alpha glucose during the oxidation is negligible because the beta form is oxidized so rapidly.

In order to estimate the approximate value for the constant representing the oxidation of alpha glucose directly, it was assumed that the value of k_1 is equal to the constant representing the conversion of alpha glucose to beta glucose. By substituting the value of k_1 determined from mutarotation data, the following equation is obtained

$$k+0.00052 = \frac{1}{t} \log \frac{A}{A-x}.$$

The value of k is based on the assumption that a constant amount of the oxidant was present at all times. If this amount be a, then $k=ak_a$, where k_a is the constant for the oxidation of the alpha form of the sugar in the presence of a molar solution of the active oxidant.

TABLE 7.—*Correlation of rate of oxidation of α-d-glucose with concentration of free bromine* [1]

Experiment No.	α-d-glucose	B [2] (Bromide)	C [3] (Bromine)	Free bromine (calculated)	HBrO (calculated)	Oxidation after—			k_1+ak_a	ak_a	k_a
						30 minutes	60 minutes	120 minutes			
	1	2	3	4	5	6			7	8	9
	Moles per l	*Equivalents per l*	*Moles per l*	*Moles per l*	*Moles per l* $\times 10^{-4}$	*Per cent*	*Per cent*	*Per cent*			
1	0.0496	0.555	0.56	0.101	0.88	18.9	33.1	52.2	0.00287	0.00235	0.023
2	.0496	.381	.374	.085	.94	16.6	28.8	49.1	.00254	.00202	.024
3	.0496	.195	.19	.063	1.11	15.2	27.5	46.0	.00231	.00179	.028
4	.0496	.550	.365	.051	.28	12.9	25.8	39.8	.00200	.00148	.029
5	.0496	.544	.19	.021	.08	5.8	15.3	30.6	.00113	.00061	.029
6	.0985	.390	.37	.081	.85	15.4	29.0	45.4	.00236	.00184	.023
Average											.026

[1] The results for each experiment were derived from an experiment similar to that given in Table 4. The temperatures were 0.4° C.±0.2°, except for experiment 2, which was 0.3° C.±0.3°. The calculations are based on the data given in this table except for experiment 2 which gives the averages reported in Table 4.
[2] Average bromide content, which corresponds to B in equation (4).
[3] Average bromine by $Na_2S_2O_3$ titration.

A series of results obtained by the oxidation of α-*d*-glucose with varying amounts of bromine and barium bromide is given in Table 7. The values representing the velocity constants for the total reaction are recorded in column 7 and the velocity constants representing the oxidation of the alpha sugar only are given in columns 8 and 9. The concentration of free bromine was varied by using different amounts of bromine in some cases, and in others different amounts of barium bromide. The maximum concentration of free bromine was 0.101 moles per liter, while the minimum was 0.021, and the corresponding constants (k_a) for the oxidation of alpha glucose were 0.023 and 0.029. The values of k_a are sufficiently uniform to show that the reaction rate is determined largely by the concentration of free bromine, and that the assumption that the reaction consists of two simultaneous reactions was justified.

In some of the oxidations reported in Table 7 there were small undetermined variations in the amount of bromine. In the experiments reported in Table 4 the concentration of bromine was determined at frequent intervals, and hence the velocity constants reported in Table 4 are better values than those of Table 7.

The value of (k_1+ak_α) under the conditions outlined in Table 4 is 0.00254, while the constant (k_α), representing the oxidation of α-*d*-glucose only is 0.0238. The ratio of (k_1+ak_α) to ak_β depends in part upon the value of the concentration of free bromine, a. Under the conditions of the experiments given in Tables 3 and 4, $(k_1+ak_\alpha):ak_\beta::1:34$, while $k_\alpha:k_\beta::1:53$. In other words, the oxidation of the beta sugar under these specific conditions is 34 times as rapid as the total oxidation of the alpha sugar. If allowance is made for the mutarotation reaction and a small difference in the concentration of free bromine, the oxidation of the beta form is 53 times as fast as the oxidation of the alpha form.

It has been shown that β-*d*-glucose is oxidized rapidly, while α-*d*-glucose is oxidized much more slowly; the marked difference in the reaction rates will now be used for ascertaining the approximate amounts of each in the equilibrium solution. The oxidation of a sugar solution containing a single isomer usually progresses uniformly, while the oxidation of a mixture of the alpha and beta forms progresses

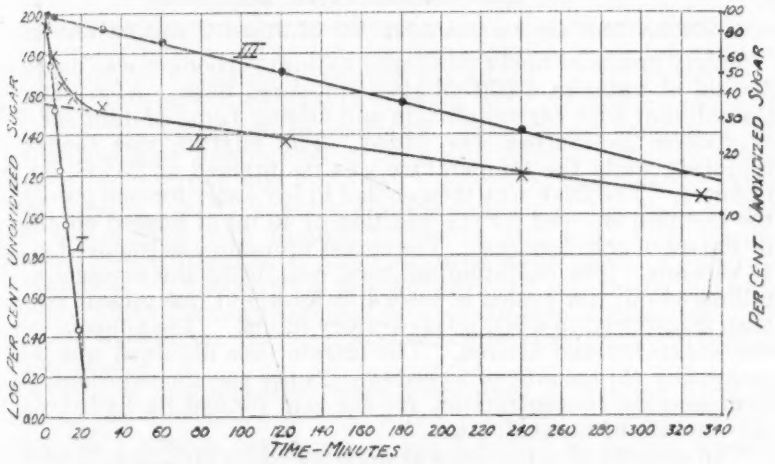


FIGURE 3.—*Bromine oxidation of d-glucose in the presence of* $BaCO_3$

rapidly until the beta is used up, and then more slowly as the oxidation of the other form is continued. Although the velocity constants for the reaction at various intervals reveal the changes in the reaction rate, the deviations are more easily detected graphically. Thus, if a pure alpha or beta sugar is oxidized with a large excess (or constant amount) of bromine and the logarithm of the per cent of unoxidized sugar is plotted against time, usually a straight line is obtained which passes through the point representing the logarithm of the initial concentration of the sugar.

This is illustrated in Curves I and III of Figure 3, which were plotted from data obtained from α-*d* and β-*d*-glucose, respectively. The slope of the curves is a measure of the reaction rate. Note that the curves are approximately linear and that they pass through the point representing the amount of the sample used. This shows that the oxidation progressed at a uniform rate throughout the experiment, which proves that the samples were homogeneous. In marked contrast,

the oxidation of an equilibrium solution proceeds rapidly for the firs 15 or 20 minutes and then more slowly. This is illustrated in Curv II of Figure 3, which gives the oxidation of an equilibrium solution o *d*-glucose. The slope of the curve increases during the first 30 minute after which the curve becomes approximately linear. The latter par of the curve represents the oxidation of α-*d*-glucose. By extendin this curve to zero time the amount of α-*d*-glucose in the solution a beginning of the reaction can be estimated. The extrapolated curv meets the axis at a point equivalent to 36 per cent. Thus, from th rates of oxidation only, it is found that an equilibrium solution o glucose contains approximately 64 per cent beta and 36 per cent alph glucose. These values are in qualitative agreement with the value (65 and 35, respectively) determined from the optical rotation of th equilibrium solution. This is additional evidence that an equilibriu solution of glucose consists largely of a mixture of the normal alph and beta forms of the sugar.

IV. EXPERIMENTAL DETAILS

1. OXIDATION OF β-*d*-GLUCOSE TO GLUCONIC DELTA LACTONE

Thirty grams of finely powdered barium carbonate was mixed wit 200 ml of water in a 500 ml glass-stoppered flask. After saturatin the solution with carbon dioxide and adding 10 ml of bromine, 9 g o crystalline β-*d*-glucose was added. The mixture was shaken con- tinuously while the temperature was maintained at 25° C. for thre minutes. The flask was then cooled in ice water for one minute, an the reaction stopped by the addition of 40 ml of linseed oil dissolve in 100 ml of cold benzene. The excess bromine was removed in abou 15 seconds. The oxidation mixture, containing the benzene solutio of linseed oil, was cooled in ice water for about one minute more an then transferred to a 500 ml separatory funnel. The aqueous solutio was separated and filtered. The filtrate thus obtained was used fo measuring (1) amount of oxidation, (2) the specific rotations, (3) th hydrogen-ion concentrations, (4) the acid formed by hydrolysis, an (5) the rate of saponification.

The amount of oxidation was determined by boiling a 10 ml sampl of the solution containing the oxidation product with Benedict' copper sulphate reagent. The cuprous oxide was estimated by Scales method [21] modified by changing the time of boiling from three to six minutes. The solutions were standardized with solutions of dextros containing like concentrations of barium bromide. The result showed that the solution of the oxidation product contained 1.0 mg/ml of reducing substance calculated as dextrose. This is equiva- lent to 2.5 per cent; that is, the oxidation of the sugar was 97.5 pe cent complete.

In order to prove that the product of the oxidation consists almos exclusively of the delta lactone, a sample of delta lactone was studie under conditions as nearly like the conditions of the oxidation experi- ments as possible. The sample of the delta gluconic lactone (8.9 g) was added to a solution of barium bromide (16.46 g of $BaBr_2 \cdot 2H_2O$) in 200 ml of water containing 30 g barium carbonate in suspensio and saturated with carbon dioxide. The solution was shaken thre minutes at 25° C., cooled, and filtered, and the filtrate used fo comparison with the oxidation products.

[21] Scales, J. Ind. Eng. Chem., vol. 11, p. 747, 1919.

The specific rotations of the oxidation products and of the solution containing the delta lactone were measured in a 2 dm water-jacketed tube, with a Bates saccharimeter. The values given in Table 1, page 339, were calculated from the following formula:

$$[\alpha]_D^{20} = \frac{^\circ S \times 0.3462 \times 207.8}{2 \times 8.9}$$

The weight of the lactone in each case was 8.9 g and the volume of the solution 207.8 ml. This volume was determined by measuring the volume of a solution containing 8.9 g of delta lactone, 16.46 g of barium bromide, and 200 ml of water. The results are given in Table 1.

Hydrogen-ion concentrations of the solutions containing the delta lactone and the solutions containing the oxidation products were measured at 25° C. with a quinhydrone electrode in the usual manner. The results are given in Table 1.

The acid formed by hydrolysis was determined in the following manner: A 10 ml sample of the oxidation solution was diluted with an equal quantity of water and heated to boiling to remove the dissolved carbon dioxide. The solution was cooled to room temperature and 25 ml of $N/10$ barium hydroxide was added. After five minutes the excess barium hydroxide was titrated with $N/10$ sulphuric acid, using phenolphthalein as an indicator. The 10 ml sample of the oxidation product neutralized 22.47 ml of $N/10$ alkali. The total volume of the solution was 207.8 ml, hence there was 0.0467 mole of lactone present. A 10 ml sample of the solution of the delta lactone which was shaken with barium carbonate and treated in manner analogous to the oxidation product required 22.48 ml $N/10$ alkali for neutralization. The oxidation product required practically the same amount of alkali for neutralization as the sample of the lactone. The agreement shows that the sugar was converted nearly quantitatively into the lactone.

The rates of saponification were determined at various times by measuring the unchanged lactone which remained after shaking the solution with barium carbonate in the presence of carbon dioxide. From time to time samples were taken; the excess barium carbonate was removed by filtration and the filtrate freed from CO_2 by boiling. Then an excess of $N/10$ barium hydroxide was added and the amount of alkali used in saponifying the lactone was determined by back titration with $N/10$ acid. The results, which are given in Table 2 and illustrated in Figure 1, show that the oxidation products derived from α- and β-*d*-glucose and the equilibrium solution are saponified at approximately the same rate as the delta lactone. The sample of the oxidation product from beta glucose, after 24 hours, required only three drops of $N/10$ alkali to produce a permanent pink coloration with phenolphthalein, while one drop of $N/10$ alkali was sufficient for the sample of the solution of the delta lactone.

As additional evidence for the presence of the delta lactone in the oxidation product, the lactone was separated as soon as possible from the solution obtained by the oxidation of β-*d*-glucose. The experimental conditions were such that the crystalline product could not have been formed from the acid by spontaneous lactone formation. The oxidation was conducted in the following manner: About 15 g of finely powdered barium carbonate was mixed with 9 g of crystalline

β-*d*-glucose. The dry mixture was added in portions while stirring to a mixture of 5 ml of bromine and 20 ml of ice water. The reaction was allowed to continue for five minutes, then 10 ml of amylene dissolved in 50 ml of cold dioxane was added and the solution shaken until all of the bromine had combined with the amylene. The dioxane solution, which contained a portion of the product, was decanted from the aqueous sirup which had separated. The aqueous residue was extracted several times with fresh portions of dioxane. The lactone is difficultly soluble in dioxane and care must be taken to secure complete extraction. After filtration a few drops of the dioxane solution on evaporation gave crystalline gluconic delta lactone. This product was separated within one-half hour after the beginning of the experiment. The remaining dioxane solution was evaporated quickly in high vacuo to a sirup. The sirup was transfered to a small breaker and the solution saturated with anhydrous ether and seeded with some of the delta lactone which was obtained as noted above; crystallization began immediately. After one hour the product was separated and dried. About 5 g of nearly pure gluconic delta lactone was obtained. After recrystallization the product melted at 152° C., and 2.5 minutes after solution gave $[\alpha]_D^{20} = +65.7°$, which decreased in 400 minutes to +7.0° (0.9654 g dissolved in 25 ml).

2. OXIDATION OF α-*d*-GLUCOSE TO GLUCONIC DELTA LACTONE

A sample of α-*d*-glucose was oxidized in manner analogous to that given for β-*d*-glucose, except that the oxidation was allowed to continue for 20 minutes at 25° C. rather than for 3 minutes. The oxidation was 85.5 per cent complete. The specific rotations and hydrogen-ion concentration are given in Table 1, page 339. The values obtained for the amount of acid formed by the hydrolysis of the oxidation product and the rate of saponification are of particular interest. A 10 ml sample of the solution of the oxidation product required for neutralization 18.0 ml of *N*/10 alkali; this is equivalent to 0.0374 moles of lactone in the product. Since the oxidation was 85.5 per cent complete, the 9 g sample of dextrose should have given 0.04275 moles of lactone. But as the reaction required 20 minutes and 5 additional minutes were consumed in removing the excess bromine and barium carbonate, some hydrolysis occurred and consequently the amount of lactone in the sample was slightly less than the amount formed by oxidation. The amount of the lactone hydrolyzed during the preparation of the sample can be estimated approximately from the rate of hydrolysis of the delta lactone. If the lactone were exposed to the hydrolytic action of the aqueous barium carbonate 15 minutes on the average, then it would be hydrolyzed approximately 10 per cent and the amount of lactone present in the sample would correspond to approximately 90 per cent of that formed by oxidation. From the foregoing the total lactone formed by oxidation is calculated as $\frac{0.0374}{0.90} = 0.0416$ mole, which is only slightly less than 0.0427, the amount which should have been formed by the oxidation. As the amount of hydrolysis can not be accurately estimated, the difference in the two values can not be ascribed, at present, to the formation of some free acid by the oxidation of the sugar. Although it is possible

that a very small portion of the sample of *α-d*-glucose, or a form of the sugar derived therefrom, is oxidized by bromine water in the presence of barium carbonate to give the free acid, the results clearly show that the product of the reaction consists for the most part of the delta lactone.

3. MEASUREMENT OF REACTION RATES

The oxidations were conducted in a 1-liter, 3-neck flask equipped with a mechanical stirrer. The stirrer was inserted in the center neck, while a tube for admitting carbon dioxide was inserted in one of the outer necks. The third neck was used for introducing the sugar sample and for withdrawing samples of the reaction mixture. At other times it was kept closed with a stopper carrying a thermometer. The reaction flask was placed in an ice bath and the solution in the flask and the ice water were stirred continuously. The solution of the salt containing 15, 30, or 45 g of $BaBr_2 \cdot 2H_2O$ in sufficient water to make 500 ml and 30 g of barium carbonate was saturated with carbon dioxide and 5, 10, or 15 ml of bromine was added. After mixing for a few minutes 4.5 g of the crystalline sugar was introduced through one of the outer necks in the flask. The mixture was stirred continuously and carbon dioxide, previously bubbled through bromine water, was slowly passed through the solution. Time was measured from the moment that the sugar was added. In the oxidation of the equilibrium solution a portion of the water ordinarily used for preparing the bromide-bromine solution was used for dissolving the sugar. The sugar solution in equilibrium was then added in place of the crystalline sugar. Samples of the reaction mixture were withdrawn at various times and the oxidations of these were stopped quickly by the addition of about 10 ml of linseed oil dissolved in 20 ml of benzene. The amount of unoxidized sugar was determined by reduction of Benedict's copper sulphate reagent. The total bromine was determined by titration of samples of the oxidation mixtures with standard sodium thiosulphate in the usual manner.

The total bromide at any moment is equal to that added plus two equivalents for each mole of sugar oxidized. The average bromide content during the reaction (B in equation (4)) was calculated from the mean amounts of bromide present between observations, multiplying each mean by the time interval for which it was the average, and dividing the sum of the products by the total time covered. The bromide content (B) which is expressed in equivalents of bromide is different from the bromide concentration ($\overline{Br}$) which represents the actual concentration of the bromide ion or molecule. The volume at the beginning of the reaction was determined experimentally, and the volume at the end was estimated from the increase in the volume of a similar solution upon the addition of the amount of barium bromide formed in the reaction. It was assumed that the variation at intermediate points was proportional to the amount of oxidation.

The results are given in Tables 3, 4, 5, 6, and 7. The velocity constants are based on the amount of sugar as determined by analysis, taking into account the change in the volume of the solution. The first experimental determination was taken as the starting point because in this way errors incident to the preparation of the solution and to the analysis are largely eliminated.

4. MEASUREMENT OF MUTAROTATION OF α-*d*-GLUCOSE AT 0° C.

A pipette holding 38.53 g of water at 0° C. was emptied into a flask in which 1.6832 g of α-*d*-glucose had been placed. When all the sugar had dissolved, a 2 dm water-jacketed tube, which had been previously cooled to about 0° C., was filled with the solution. The rotations observed with a Bates saccharimeter at various times after solution were: 27.10° S. (4 minutes); 27.06° S. (6 minutes); 26.71° S. (19 minutes); 26.13° S. (40.5 minutes); 24.40° S. (121 minutes); and 22.09° S. (240 minutes). Twenty-four hours later the solution gave a constant reading of 12.88° S. The temperature of the solution was 1.5° ± 0.5°. The density as determined at 2° C. with a picnometer was 1.0176 g/ml.

The velocity constants were calculated by the usual formula:

$$(k_1+k_2)=\frac{1}{t}\log\frac{r_0-r_\infty}{r_t-r_\infty}$$

The average value so obtained for (k_1+k_2) was 0.00080. The amounts of alpha and beta glucose in the equilibrium solution were calculated from the specific rotations of alpha and beta glucose and of the equilibrium solution. The values used [23] for these quantities were $[\alpha]_D^{20}=+113.4°$, $+19.7°$, and $+52.2°$, respectively. These values give $\frac{k_1}{k_2}=1.883$, from which k_1 was determined as 0.00052 at 1.5° C. All logarithms in the paper are expressed to the base.

V. APPLICATION OF THE METHOD

It is believed that the experimental methods which are described in this and the previous publications can be used for studying the various active forms of the sugars in solution and for determining some of the pertinent questions relating to the composition of sugar solutions. For instance, it has been shown previously [23] that the equilibrium between the various forms of *d*-gulose may be varied by the addition of calcium chloride. Such changes in the equilibrium may be followed by measuring the reaction rate. Also the rotation of the at present unknown β-*d*-gulose may be estimated from the composition of the solutions, together with the optical rotation of the alpha form. The oxidation method is being applied also to the products obtained from the various saccharides by enzyme hydrolysis to ascertain the substances formed. Oxidations are being conducted on the alpha and beta forms of the principal sugars in order to determine whether their solutions react solely as mixtures of the alpha and beta forms, or whether the oxidations reveal the presence of one or more additional substances. These studies are being made under strictly comparable conditions so that they will form an adequate basis for the comparison of the reactivity of the various isomeric forms of different sugars.

WASHINGTON, January 11, 1933.

---

[23] International Critical Tables, vol. 2, p. 347.
[23] Isbell, B. S. Jour. Research, vol. 5 (RP226), p. 741, 1930.

RP535

SCATTERING OF ELECTRONS BY IONS AND THE MOBILITY OF ELECTRONS IN A CÆSIUM DISCHARGE

By C. Boeckner and F. L. Mohler

ABSTRACT

The mobilities of electrons in the positive column of a cæsium discharge are derived from measurements of the electrical gradient and the electron temperature and concentration. The value of the cæsium atom cross section, estimated from the mobilities at small electron concentrations, is 3.3×10^{-16}cm² for electron energies of about 0.33 volt. The cross section apparently increases linearly with the concentrations of ions in the discharge. The variation is found to be due to the scattering of the electrons by ions. The value of the ion cross section can be evaluated from the rate of variation; it is 75×10^{-16}cm² for 0.33=volt electrons. This magnitude can be explained by the electrostatic interaction between the ions and electrons.

CONTENTS

	Page
I. Introduction	357
II. Method	357
1. Theory	357
2. The discharge tube	358
3. The measurements	358
III. Results	359
IV. Sources of error	361
V. Discussion	361

I. INTRODUCTION

Some recent work by T. J. Killian [1] shows that atomic electron scattering areas can be evaluated from the electrical characteristics of the positive column of a gas discharge. The method involves the measurement of the electron temperature, concentration, and the electrical gradient by means of the familiar Langmuir probe technique. Some measurements of this type by one of the authors have shown that the scattering area of the cæsium atom apparently increases with the discharge current. The present investigation was undertaken in order to find the reason for this unexpected behavior. The explanation was found to lie in the unusually large scattering area of the cæsium ion, due to its Coulomb force field. In a cæsium discharge at low pressures and high currents, the ions play a more important rôle in electron scattering than the atoms.

II. METHOD

1. THEORY

The mobility of a cloud of electrons drifting through a gas under the influence of an electric field of intensity X is defined by the relation

$$K = \frac{u}{X} \tag{1}$$

[1] T. J. Killian, Phys. Rev., vol. 35, p. 1238, 1930.

where K is the mobility and u is the average velocity of the electrons in the direction of the field. The current density I of the charge carried by the electrons is equal to Neu where N is the number of electrons in a cubic centimeter and e is the electronic charge.

Langevin [2] has derived the following expression for the mobility. It is correct if the atom can be assumed to behave as an elastic sphere in collisions with an electron.

$$K=\frac{I}{NeX}=\frac{3}{8}\pi^{\frac{1}{2}}\frac{e}{(2mkT)^{\frac{1}{2}}}\frac{1}{\overline{A}} \tag{2}$$

Here m is the mass of an electron and T is the electron temperature; k is Boltzman's constant. $\overline{A}$ is the total cross-sectional area in unit volume of the atoms obstructing the diffusion. If there is only one type of atom, then $\overline{A}=N_0A_0$ where N_0 is the number in the unit volume and A_0 is the "cross-section area" of the atom. If there are in addition N_+ ions of area A_+, $\overline{A}$ is given by the relation [3]

$$\overline{A}=N_0A_0+N_+A_+ \tag{3}$$

It is seen from equations 2 that $\overline{A}$ may be evaluated from measurements of I, X, N, and T.

In deriving the above expression for the mobility, it is assumed that the concentrations of ions and electrons are constant in space. In the discharge tube this concentration varies considerably over the cross section of the tube. It can be shown, however, that the values of the atomic areas computed will not be greatly in error if the average values of the current and electron and ion concentration over the tube cross sec tion are used in the equations.

2. THE DISCHARGE TUBE

The discharge tubes employed for the measurements were about 30 cm long and 1.8 cm in diameter. An oxide coated platinum ribbon which could be heated electrically was used as cathode. The anode was a platinum cylinder. The tubes were baked out at 400° C. and the cæsium distilled into the tube. A cæsium vapor discharge was maintained for several hours or longer before the tubes were sealed off from the pumps. During some of the work the tubes were connected to the pumps while the measurements were being made.

3. THE MEASUREMENTS

The probes used in the electrical measurements were platinum wires 0.4 and 1.0 mm in diameter; the sides were insulated by glass tubing and the flat ends were exposed to the discharge.

The electron temperature was derived from the slope of the straight line obtained by plotting the logarithm of the electron current to the probe against the probe potential. The temperature is given by the relations

$$T/11{,}600=V_0=(V_2-V_1)\ \text{log.}\ e/(\log I_1-\log I_2)$$

[2] Thomson, "Conduction of Electricity through Gases," 3 ed., p. 170.
[3] See reference 2, p. 171.

I_1 and I_2 are the electron currents at potentials V_1 and V_2 and V_0 is two-thirds the average electron energy in volts.

The electron concentration was derived from the magnitude of the saturation electron current density to the probe when the latter was positive to the discharge.

$$N = 4.03 \times 10^{13} i_0 / T^{1/2}$$

i_0 is the saturation electron current divided by the prove area.

The axial electrical gradient was obtained from the difference in potential between two similar probes placed about 10 cm apart along the axis when they were drawing equal electron currents.

Most of the probe surfaces were located at the axis of the discharge tube. The average value of the electron concentration over a cylindrical discharge tube is, according to Tonks and Langmuir,[4] equal to 0.70 times the value at the axis. At high pressures this factor drops to 0.42. A few measurements of the distribution of the electron concentration across the discharge tube showed, however, that the former factor was more nearly correct even at the higher of the pressures used. The factor 0.70 was therefore used in all of the computations to convert the measured concentration at the axis to the average value over the discharge.

The current density, I, of equation (2) was taken to be the discharge current divided by the tube area.

The ion concentration is difficult to measure directly. Its value was taken to be that of the electrons, a relation which must be true to a high degree of accuracy.

The cæsium vapor pressure was computed from the temperature of the cæsium by means of the equation.[5]

$$\log P = -3{,}966/T + 7.1650$$

The number of atoms in unit volume was derived from the vapor pressure and the temperature of the discharge tube wall as determined by a thermocouple in contact with the glass.

For further details concerning the probe measurements and characteristics of the cæsium positive column, a recent paper by one of the authors should be consulted.[6]

III. RESULTS

Figure 1 shows a plot of the total cross section of atoms and ions divided by the number of atoms against the ion concentration, N_+. The ordinates are therefore from equation (3)

$$\frac{\overline{A}}{N_0} = A_0 + N_+ \frac{A_+}{N_0}$$

The curves obtained should be straight lines as is observed. It is obvious from the equation that the intercept of the line on the vertical axis is A_0, the cross section of the atom. The cross section of the ion can be derived from the slope of the line, A_+/N_0. Table 1 gives values of A_+ and A_0 derived in this way at various cæsium pressures.

[4] Tonks and Langmuir, Phys. Rev., vol. 34, p. 876, 1929.
[5] Rowe, Phil. Mag., vol. 3, p. 534, 1927.
[6] F. L. Mohler, Collisions of the First and Second Kind in the Positive Column of a Cæsium Discharge, B. S. Jour. Research, vol. 9 (RP484), p. 493, October, 1932.

Column 3 gives the value of the electron energy in volts, V_0. Column 2 gives the number of cæsium atoms in unit volume at the pressure and temperature of the measurements.

It is seen that the ion cross section decreases with the electron energy while the cross section of the atom increases. The value of 3.3×10^{-14} for the atom at the higher electron temperatures does not differ greatly from the value given by Brode of 3.1×10^{-14}cm² for

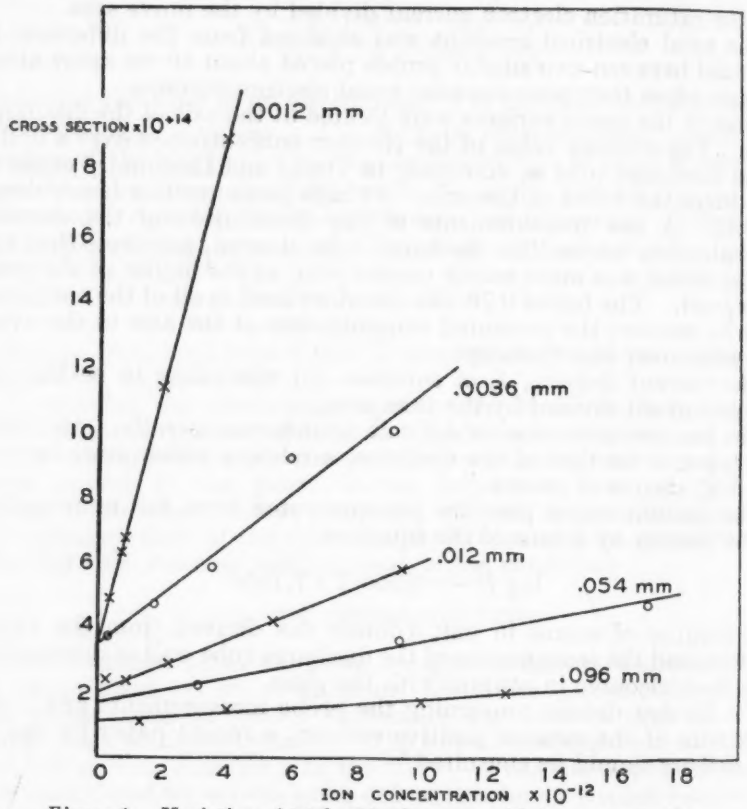


Figure 1.—Variation of total scattering area with ion concentration

Ordinates: Total scattering area per cm³ divided by the number of atoms; abscissæ, average ion concentration in ions per cm³.

electrons having the uniform energy of 0.6 volts. This latter value was obtained by a direct type of measurement.[7]

TABLE 1

Cs pressure	Number of atoms in cm³	Electron energy	Ion cross section	Cs atom cross section
mm	$\times 10^{14}$	*Volts*	$\times 10^{-14}$cm²	$\times 10^{-14}$cm²
0.065	12	0.222	134	1.4
.027	5.0	.235	117	2.0
.013	2.4	.263	98	2.4
.0060	1.1	.282	87	3.3
.0036	.67	.333	75	3.3
.0012	.22	.400	60	2.9

[7] Brode, Phys. Rev., vol. 34, p. 673, 1929.

Results at higher pressures than those tabulated show that the atom cross section falls off very rapidly with decreasing electron speed. Though measurements at these pressures are perhaps not trustworthy, it is interesting to note that such a rapid decrease in cross section with electron speed at low electron energies is predicted by the quantum mechanics.[8]

IV. SOURCES OF ERROR

An examination of equations (2) and (3) will show that the magnitude of the ion cross section is independent of a knowledge of the absolute value of the cæsium pressure or of the ion and electron concentration. It depends only upon measurements of the relative values of the electron concentrations. It should also be independent of the presence of a foreign gas in the discharge tube.

The value of the cæsium atom area on the other hand depends critically on all of these quantities. The values given in the table are the means of results obtained from a number of discharge tubes. One of the tubes yielded values of A_0 at low cæsium pressures which were almost twice as high as those given in the table. This was ascribed to the presence of foreign gas and the results were rejected. The values obtained from the measurements with the discharge tube on the pumps were in agreement with the tabulated results, though the accuracy was less because of the difficulty of knowing the cæsium temperature and vapor pressure under such conditions. Neglecting the rejected values, the mean deviation of the mean for all of the measurements was about 10 per cent.

The values of the ion cross section were, for unknown reasons, subject to larger fluctuations; the mean deviation from the mean of the results from a large number of discharge tubes was 20 per cent.

Another source of error involves the fact that the mobility equations of Maxwell and Langevin assume that the electrons have a Maxwellian velocity distribution in a system of coordinates moving with a velocity equal to the average electron velocity. The fact that the velocity distribution is actually Maxwellian is proven by the "straightness" of the plots of the logarithm of the electron probe current against the probe potential. Whether or not the perturbation of the velocity distribution due to the electrical field has the theoretical form is impossible to ascertain. The magnitude of the deviations is too small.

As mentioned above, an important source of error is the radial variation of ion and electron concentration across the discharge. Simple considerations show, however, that the values of the atom cross section will be correct if the average values are used in the mobility equation. The average of the electron concentration was assumed to be 0.7, the value at the center for all pressures. The values of A_0 at the higher pressures should, therefore, be reduced somewhat (equation(2)), if this factor becomes lower as the pressure is increased. The values of the ion area are, however, in error due to the use of average values. Detailed consideration shows that the curves of Figure 1 should not be straight, but should have a slight curvature.

[8] Quantum Mechanics of Collision Processes, P. M. Morse, Reviews of Modern Physics, vol. 4, p. 577, 1932.

The ion area, derived from the slope at zero ion current, should be multiplied by the Langmuir-Tonks factor, 0.70. Due to various uncertainties such a correction was not applied.

V. DISCUSSION

Maxwell and Langevin have given expressions for the mobility for laws of the force between the particles which vary as some inverse integral power of their mutual distance. The equations are supposedly exact if the drifting particles (electrons) have a small mass compared to those obstructing the drift. This is of course the case of interest here. Another requirement is that the effects of multiple collisions be negligible.

The Langevin equation for the inverse square law of attraction is as follows: [9]

$$K=\frac{6}{32\pi^{1/2}}\frac{(2kT)^{3/2}}{N_+e^3m^{1/2}\int_0^\infty \sin^2\theta a da} \tag{5a}$$

Here $a=mv^2b/e^2$, v is the electron velocity, and θ is the half of the angle of deflection of an electron whose initial line of approach passes within a distance, b, of the ion. For the inverse square law of force [10] $\sin\theta=1/(1+a^2)^{1/2}$, so that the integral in equation (5a) becomes $0.5\log_e(1+a^2)$. The definite integral therefor becomes infinite and the mobility is zero. A definite value of the mobility can be obtained if all collisions are neglected in which the electron is at a greater distance from the ion than the mean distance between the ions; that is, $1/N_+^{1/3}$. This is a reasonable procedure since the effects of all of the ions on an electron at distances greater than this will mutually annul each other. The assumption is equivalent to changing the upper limit of the integral to a value of a given by the relation

$$a_1=mv^2/e^2N_+^{1/3} \tag{4}$$

The mobility then becomes

$$K=\frac{12}{32\pi^{1/2}}\frac{(2kT)^{3/2}}{N_+e^3m^{1/2}\log_e[1+(mv^2/e^2N_+^{1/3})^2]} \tag{5}$$

The relation given by Maxwell [11] is almost identical, the numerical coefficient, $2/\pi^{3/2}$, being however about 1.7 times that of Langevin. It should be remarked that the mobility is very insensitive to changes in the value of a_1 of equation (4); a change of tenfold producing only a 40 per cent change in K when $N_+=10^{13}$ (a value representative of conditions in the present experiment).

To compare the theoretical mobility with the observed, it is convenient to obtain an expression for the cross section area of a sphere which would yield the same value of the mobility according to equation (2) as results from the Coulomb law of interaction according to equation (5). This area is the value of A_+ of equation (3). It is easily found to have the form

$$A_+=\frac{\pi}{4}\frac{e^2}{V_0^2}\log_e[1+(mv^2/e^2N_+^{1/3})^2] \tag{6}$$

[9] See reference 2, p. 170.
[10] See reference 2, p. 167.
[11] Richardson, The Electron Theory of Matter, p. 420, 1914.

where kT is replaced by eV_0. The quantity mv^2 in the logarithmic term may be replaced without appreciable error by $2eV_0$. The Maxwell theory yields an expression with a smaller numerical coefficient, $3\pi^2/64$.

With N_+ put equal to 10^{13} and V_0 having a value equivalent to 0.3 volt, one obtains for A_+ a value of 170×10^{-14} cm². The value corresponding to the numerical factor of Maxwell is 110×10^{-14}. Both are larger than the observed value 84×10^{-14} cm². The agreement is perhaps as good as can be expected from the uncertainties in both the measurements and the theory.[12]

From equation (6) it is seen that the ion area should vary inversely as the square of the electron temperature or V_0. The observed variation with temperature is less rapid than that predicted by this relation though the results at higher pressures obey it approximately.

The variation with temperature makes it apparent that the effect of ions will be difficult to observe in discharges in most other gases. The electron temperature in other gas discharges is usually some 10 times greater than in a cæsium vapor discharge; the ion area should therefore be 100 times smaller. The scattering due to ions should only be observable for very low pressures and high currents or when the gas atoms have a small scattering area.

WASHINGTON, January 16, 1932.

[12] The theory given above is obviously defective in that it fails to take into account rigorously distant collisions of an electron with two or more ions. L. H. Thomas, Proc. Roy. Soc., vol. 121, p. 478, 1928, has obtained an expression for the mean loss of momentum of an electron traveling through an ion gas in which an attempt has been made to allow for such distant collisions. If one follows Langevin in assuming that the electrons have a Maxwellian velocity distribution in a coordinate system moving with the average electron velocity it is possible to evaluate from the Thomas expression the total loss of momentum of the electrons in unit time. If this is equated to the momentum gained from the field, an expression is obtained for the mobility. It differs from that of equation (5) in that the numerical coefficient is smaller and that the logarithmic term is replaced by another which happens, however, to have the same numerical value to within a few per cent. The ion area obtained is larger than any given above, 380×10^{-14} cm².

THE PREPARATION OF OPTICALLY STABLE SUGAR SOLUTIONS FOR COLORIMETRIC ANALYSIS[1]

By J. F. Brewster and F. P. Phelps

ABSTRACT

The successful application of colorimetry in the sugar industry is dependent upon the development of a satisfactory technique for preparing sugar solutions having a satisfactory degree of transparency. In the present paper existing methods have been revised. The process of clarification has been shortened and the transparency of the solutions improved. These results have been accomplished by increasing the concentration of the dry substance or total solids, dissolving and filtering the sugar products hot, and developing the application of better filters. In addition, other details of manipulation have been improved.

CONTENTS

		Page
I.	Introduction	365
II.	Filters	366
III.	Calculation of weights	367
IV.	Preparation and filtration of the sample	367
V.	Dilution of color	368
VI.	Comparison of procedures	368
VII.	Appendix. Table 2.—Densities of pure sucrose solutions	370

I. INTRODUCTION

Peters and Phelps[2] in an earlier publication, hereinafter referred to as T338, have described methods used in the preparation of sugar solutions for colorimetric analysis and have discussed the optical properties of sugar solutions, particularly with reference to the effect of turbidity upon color measurement. They found that uncontrollable errors of varying magnitude result from turbidity and that Beer's law does not hold for turbid solutions. In order to secure the necessary degree and stability of transparency, advantage was taken of the protective action of sucrose in concentrated solution toward the turbidity-producing colloids. The solutions were so prepared as to have as high a concentration of total solids or dry substance (d. s.) as was compatible with a reasonably rapid filtration rate with the filtering apparatus then available and at the same time avoid crystalization. The dry substance (d. s.) concentration was placed at about 0.70 g per ml, corresponding to approximately 55 Brix. The solutions were then filtered through pads of purified asbestos.

More recent experience, especially with hard white sugars, has shown that a more satisfactory and more stable degree of transparency is obtainable for this class of sugars if the dry substance concentration be made much higher. In the present paper it is therefore recommended that this never be lower than 60 Brix (about 0.77 g per ml) and without disadvantage may be higher. The samples of sugar product are to be dissolved and diluted with the aid of heat and

[1] Presented in part before the sugar division of the American Chemical Society at Swampscott, Mass., September, 1928, under the title "The Spectrophotometry of White Sugars."
[2] H. H. Peters and F. P. Phelps, B. S. Tech. Paper No. 338, Pt. II, March, 1927.

filtered warm. Filtering apparatus with greater filter area than that formerly used for retaining the asbestos is also described so that the process of clarification is hastened. A method for the dilution of color with dry colorless sugar is also described.

II. FILTERS

Two filters with pads of purified asbestos are to be prepared before the sugar solution is made up. Various forms of filters are suitable. Among these the 25 ml Gooch crucibles fitted with a disk of 200-mesh bolting silk, as recommended in T338, page 211, is convenient and low priced. Greater filter area may be similarly obtained by fitting a 10 cm glass funnel with a 4 cm perforated porcelain plate which is then covered with 200-mesh bolting silk as above. Because of convenience and cleanliness Jena filters in the form of cylindrical funnels, 60 or 120 ml capacity with 4 cm fritted glass filter disks, have been found most satisfactory. The largest pore size, No. 1, is used for preliminary, and No. 3 which is much finer, for the final filtration. The pores of the latter frequently become clogged with fine asbestos which retards filtration. The intermediate pore size, No. 2, allows the passage of fine asbestos which, however, usually ceases after several washings with water and the filtration of 100 ml or less of high density sirup. This size as well as the No. 1, after careful preparation of the pads, has been successfully used for the final filtration.

When forming the pad, regardless of what form of filter is employed, the asbestos is sucked down by means of the aspirator and packed tightly by tamping with a blunt stirring rod to produce a layer about 0.5 cm thick. The pad is then washed several times with water (See T338, p. 271.) Equally good clarification has been obtained with XXX, XX, or A grade asbestos. The finer-fibered grades B and C give satisfactory filtration, but there is greater difficulty in washing out the acid used in purification. A rapid method for purifying asbestos has been described elsewhere.[3]

Diatomaceous earth has been used, especially in Europe, as an aid in clarifying sugar solutions for colorimetric analysis. Mastalir[4] has recently shown that this material has a decided decolorizing effect upon molasses solutions.

Working with a 60 Brix solution of washed raw sugar rendered transparent by two filtrations with asbestos, the present writers twice repeated the filtration with purified standard filter cel (1 per cent by weight of dry substance) and observed the following decrease in $-\log t$ at wave length 560: Asbestos filtrate, $-\log t = 0.236$; first filter cel filtrate, $-\log t = 0.216$; second filter cel filtrate, $-\log t = 0.166$. A corresponding decrease was observed at four other wave lengths. Because of this decolorizing action, diatomaceous earth, even in the improved forms now available, is not regarded as being suitable for the clarification of sugar solutions that are to be subjected to colorimetric analysis. Peters and Phelps (T338, p. 269), after trying the best grades of Kieselguhr then available, rejected this material because it not only decolorized but also acted selectively, causing a change in the slope of the absorption curve.

---

[3] J. F. Brewster and F. P. Phelps, J. Ind. Eng. Chem. (Analyt. ed.), vol. 2, p. 373, 1930.
[4] V. Mastalir, Zeit. Zuckind. Cechosl. Rep., vol. 56, p. 337, 1931-32.

III. CALCULATION OF WEIGHTS

A generous supply of turbid solution should be available, the amount to be prepared depending upon the capacity of the optical cells employed. Time is saved by preparing a definite weight of solution having a definite, predetermined Brix which may be satisfactorily approximated by using a rough balance. No fractional gram weights are used except in the case of very dark products that require dilution of color. These will be considered in a later section. The required weights of sample and water may be calculated as follows:

$$\frac{\text{Weight of solution required} \times \text{Brix of solution}}{\text{Brix of sample}} = \text{weight of sample to be taken.}$$

Weight of water to be added = weight of solution − weight of sample. The Brix of dry sugars may be assumed to be 100. In the case of nearly dry products of relatively high purity such as 96 test raw sugars, a sufficiently close approximation results if polarization be substituted for Brix of sample in the denominator of the above fraction.

The transparency of thin liquors may be improved by the addition of an amount of sucrose, previously tested and found to be colorless, sufficient to increase the Brix to 60 or higher. The weight of water in this case remains constant and the formula for calculation may be written:

$$\frac{\text{Weight of solution required} \times (100 - \text{Brix of solution})}{100 - \text{Brix sample}} = \text{weight of sample.}$$

Weight of solution − weight of sample = weight of sucrose to be added.

IV. PREPARATION AND FILTRATION OF THE SAMPLE

The calculated amount of sample to provide a solution of 60 to 65 Brix is weighed in a tared flask and weights equivalent to the required amount of water are added to the pan. The flask with contents is placed in a water bath heated to 80° to 90° C. and hot distilled water is added in small quantities at a time, the flask being shaken to promote quick solution and to insure a high concentration. To guard against over dilution the flask dried on the outside is occasionally placed on the balance pan.

When solution is complete and the required amount of water has been added, purified asbestos (grade A) in amount equal to about 0.5 per cent of the solution is added. The flask is then closed with a clean rubber stopper, and vigorously shaken. The flask is returned to the warm bath and the preliminary filter is heated by rinsing with hot distilled water which is drawn off as thoroughly as possible by suction. A few milliters of the warm solution are poured on the pad and drawn through to displace water. The main portion of the solution, or as much as the filter will hold, is added and after a few drops have filtered the suction is stopped and a clean receiver is substituted. The pads are to be kept covered with solution during filtration, at the end of which the suction is stopped before the pad becomes uncovered. The receiver is detached and returned to the bath while the second filter is being rinsed with hot water and drained.

156547—33——6

The second filtration is performed exactly as the first, no asbestos being added to the first filtrate. The main portion of the filtrate is collected in a clean receiver. This filtrate is cooled and adhering water wiped from the neck of the bottle which is then closed with a clean, dry stopper and shaken to mix the contents thoroughly. The refractometric Brix of the optically clear filtrate is determined and c (=g dry substance per ml) obtained by reference to Table 2 (Appendix). The solution is now ready for colorimetric examination. With properly prepared solutions and filters further filtration is of doubtful value unless some scattered particles of asbestos have passed through. If the second filtrate appears turbid the best practice is to prepare a new solution with increased dry substance concentration. Jena filters are easily cleansed by removing the pads and drawing water and air through the pores by means of the aspirator connected alternately to the mouth and the stem of the funnel. This dislodges asbestos fibres, which may be poured out. Treatment of the glass filters with chromic-sulphuric acid mixture removes waxy or greasy film deposited by sugar solutions.

V. DILUTION OF COLOR

Directions are given in T338, pp. 277 and 285–286, for the dilution of very dark sugar solutions with colorless sirup in order that good photometric readings may be made and to insure a high degree of transparency. Instead of employing for this purpose a stock sirup, which may be subject to decomposition and change in storage, a high-grade, nearly colorless solid sugar may be used in the following manner: One hundred grams of the solid sugar are weighed in a tared flask. A small amount of the colored sample whose dry substance content has been determined is introduced and the whole reweighed. All these weighings should be accurate to the nearest milligram in order that the proportion of colored dry substance may be calculated. The mixture is dissolved and diluted to 60 to 65 Brix exactly as described in the foregoing section. Sugar of the quality of the highest grade refinery tablets may be used as diluent and for accurate results its absorbancy may be deducted. The specific absorptive index of good tablet sugars is less than 0.005 at wave length 560 and in many cases this may be ignored as not affecting the final results. The reference at the head of this section is to be consulted for methods of calculating colored dry substance in the mixture.

VI. COMPARISON OF PROCEDURES

In Table 1 are given for comparison results obtained by varying the dry substance concentration and the temperature at which the samples were dissolved and filtered. Four types of sugar products were used, each diluted to three different d. s. concentrations designated in column 2 as A, B, and C, corresponding, respectively, to 55, 60, and 65 Brix, the approximate concentration before filtration. The final concentration after filtration and cooling is given as refractometric Brix in column 3, and as the corresponding c in g per ml in column 4. In column 5 is given the specific absorptive index, $-\log t$, at λ 560 mμ of each solution. In column 6 are shown the differences $(-\log t \text{ A})-(-\log t \text{ B})$ and $(-\log t \text{ C})-(-\log t \text{ B})$ expressed as per cent $-\log t$ B. In column 7 the approximate

temperatures at which the solutions were prepared are given. The solutions prepared at 40° were filtered at room temperature, while those prepared at 70° were filtered at 70°.

The influence of dry substance concentration is to be seen by reference to columns 5 and 6. Regardless of the temperature at which the solutions were prepared, the highest absorption value for any given product occurs in the solution having the lowest density and is attributed to the presence of turbidity in these solutions that is not removable by the filtration method used. (Compare T388, p. 280.)

Samples 8 and 9 were prepared by dispersing the molasses in very pure sucrose solution as described in Section V. The proportion of molasses dry substance in total dry substance varied from 0.88 to 1.13 per cent and the general agreement among the results demonstrates the effectiveness of sucrose in preventing turbidity. Optical disturbance due to crystallization in 70 Brix sugar solutions has never been encountered and it is therefore inferred that many high density refinery or factory liquors may be prepared for colorimetric analysis without further dilution.

TABLE 1.—*Comparison of procedures*

Sample No.	Designation of solution	Brix by refractometer	c in g/ml	$-\log t$ λ 560	Difference per cent on $-\log t$ B	Approximate temperature of solution
1	2	3	4	5	6	7
						° C.
1	A	55.2	0.6948	0.0213	+10.40	40
	B	61.3	.7933	0.0193		70
	C	66.4	.8800	.0199	+3.11	70
2	A	56.0	.7074	.0458	+3.62	40
	B	61.4	.7940	.0442		40
	C	66.3	.8780	.0440	−.45	40
II. WASHED RAW SUGARS						
3	A	55.1	0.6533	0.349	+26.29	70
	B	60.7	.7834	.275		70
	C	67.0	.8064	.276	+.36	70
4	A	55.4	.6979	.300	+41.51	40
	B	61.0	.7883	.212		40
	C	68.8	.9217	.208	−1.89	70
5	A	57.5	.7313	.244	+5.18	70
	B	60.1	.7735	.232		70
	C	69.6	.9359	.234	+.85	70
III. RAW SUGARS (UNWASHED)						
6	A	55.2	0.6948	1.224	+9.29	40
	B	61.4	.7949	1.120		70
	C	71.8	.9754	1.105	−1.34	70
7	A	55.1	.6932	1.201	+19.99	70
	B	61.4	.7949	1.001		70
	C	70.3	.9483	1.000	−.10	70
IV. MOLASSES						
8	A	55.7	0.7027	33.10	+2.48	70
	B	60.5	.7801	32.30		70
	C	66.1	.8750	32.82	+1.55	70
9	A	56.2	.7106	53.00	+.57	70
	B	61.8	.8016	52.70		70
	C	66.2	.8763	53.10	+.76	70

VII. APPENDIX. TABLE 2.—DENSITIES OF PURE SUCROSE SOLUTIONS

This table is an expansion of Table 2, B. S. Tech. Paper No. 338, page 304, and gives values corresponding to degrees Brix to cover the higher densities recommended. It is to be used for finding values of c (g dry substance per ml) corresponding to degrees Brix, density, or apparent specific gravity of sugar solutions from analytical data. The tabulated values were derived in the manner already fully described in the publication referred to above.

TABLE 2.—*Densities of pure sucrose solutions*

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
59.0	1.28059	1.27958	1.28320	75.555	64.0	1.31028	1.30927	1.31297	83.858
59.1	118	1.28017	379	.718	64.1	089	988	359	84.028
59.2	176	075	437	.880	64.2	149	1.31048	418	.198
59.3	235	134	497	76.043	64.3	209	108	479	.367
59.4	294	193	556	.207	64.4	270	169	540	.538
59.5	352	251	614	.369	64.5	330	229	600	.708
59.6	411	309	672	.533	64.6	391	290	661	.879
59.7	469	367	731	.696	64.7	452	350	723	85.049
59.8	528	426	789	.860	64.8	512	412	784	.220
59.9	587	485	849	77.024	64.9	573	473	845	.391
60.0	1.28646	1.28544	1.28908	77.188	65.0	1.31633	1.31533	1.31905	85.561
60.1	704	602	966	.351	65.1	694	594	966	.733
60.2	763	661	1.29025	.515	65.2	755	655	1.32028	.904
60.3	822	720	084	.680	65.3	816	716	089	86.076
60.4	881	779	143	.844	65.4	877	777	150	.248
60.5	940	838	203	78.009	65.5	937	837	210	.419
60.6	999	897	262	.173	65.6	998	898	271	.591
60.7	1.29058	956	321	.338	65.7	1.32059	959	332	.763
60.8	117	1.29015	380	.503	65.8	120	1.32019	393	.935
60.9	176	074	439	.668	65.9	181	081	455	87.107
61.0	1.29235	1.29133	1.29498	78.833	66.0	1.32243	1.32142	1.32516	87.280
61.1	295	193	559	.999	66.1	304	203	577	.453
61.2	354	252	618	79.165	66.2	365	264	638	.626
61.3	413	311	677	.330	66.3	426	325	699	.798
61.4	472	370	736	.496	66.4	487	385	759	.971
61.5	532	430	796	.662	66.5	548	446	820	88.142
61.6	591	489	855	.828	66.6	610	509	884	.318
61.7	651	548	915	.995	66.7	671	570	945	.492
61.8	710	608	975	80.161	66.8	733	632	1.33007	.666
61.9	770	667	1.30034	.328	66.9	794	693	068	.839
62.0	1.29829	1.29726	1.30093	80.494	67.0	1.32855	1.32754	1.33129	89.012
62.1	889	786	153	.661	67.1	917	816	192	.187
62.2	948	845	212	.828	67.2	979	878	254	.361
62.3	1.30008	905	273	.995	67.3	1.33040	939	315	.536
62.4	068	966	234	81.162	67.4	102	1.33001	377	.711
62.5	127	1.30025	393	.329	67.5	163	062	438	.885
62.6	187	085	453	.497	67.6	225	124	500	90.060
62.7	247	145	513	.665	67.7	287	186	562	.235
62.8	307	205	573	.833	67.8	349	248	625	.411
62.9	367	265	633	82.001	67.9	410	309	686	.585
63.0	1.30427	1.30325	1.30694	82.169	68.0	1.33472	1.33371	1.33748	90.761
63.1	487	385	754	.337	68.1	534	433	810	.937
63.2	547	446	815	.506	68.2	596	495	872	91.112
63.3	607	506	875	.674	68.3	658	557	935	.288
63.4	667	566	936	.843	68.4	720	619	997	.464
63.5	727	626	994	83.012	68.5	782	681	1.34059	.641
63.6	787	686	1.31055	.180	68.6	844	743	121	.817
63.7	848	747	117	.350	68.7	906	805	183	.993
63.8	908	807	177	.519	68.8	968	867	245	92.169
63.9	968	867	237	.688	68.9	1.34031	930	309	.347

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
69.0	1.34093	1.33992	1.34371	92.524	75.5	1.38220	1.38119	1.38510	104.356
69.1	155	1.34054	433	.701	75.6	285	184	575	.543
69.2	217	116	495	.878	75.7	350	249	640	.731
69.3	280	179	558	93.056	75.8	415	314	705	.919
69.4	342	241	621	.233	75.9	480	379	770	105.106
69.5	405	304	684	.411	76.0	1.38545	1.38444	1.38835	105.294
69.6	467	366	746	.589	76.1	610	510	902	.482
69.7	530	429	809	.767	76.2	675	575	967	.670
69.8	592	491	871	.945	76.3	740	640	1.39032	.859
69.9	655	554	934	94.123	76.4	805	705	097	106.047
70.0	1.34717	1.34616	1.34997	94.302	76.5	870	770	162	.236
70.1	780	679	1.35060	.481	76.6	935	835	228	.424
70.2	843	742	123	.660	76.7	1.39000	900	293	.613
70.3	906	805	186	.839	76.8	065	965	358	.802
70.4	968	867	248	95.017	76.9	130	1.39030	423	.991
70.5	1.35031	930	311	.197	77.0	1.39196	1.39096	1.39489	107.181
70.6	094	993	375	.376	77.1	261	161	554	.370
70.7	157	1.35056	438	.556	77.2	326	225	619	.560
70.8	220	119	501	.736	77.3	392	291	685	.750
70.9	283	182	564	.916	77.4	457	356	750	.940
71.0	1.35346	1.35245	1.35627	96.096	77.5	523	422	816	108.130
71.1	409	308	691	.276	77.6	588	488	882	.320
71.2	472	371	754	.456	77.7	654	554	949	.511
71.3	535	434	817	.636	77.8	719	619	1.40014	.701
71.4	598	498	881	.817	77.9	785	685	080	.892
71.5	661	561	944	.998	78.0	1.39851	1.39751	1.40146	109.084
71.6	725	625	1.36008	97.179	78.1	916	816	211	.274
71.7	788	688	072	.360	78.2	982	882	277	.466
71.8	851	751	135	.541	78.3	1.40048	948	344	.657
71.9	914	814	198	.722	78.4	113	1.40013	409	.848
72.0	1.35978	1.35877	1.36261	97.904	78.5	179	079	475	110.041
72.1	1.36041	940	324	98.085	78.6	245	145	541	.232
72.2	105	1.36004	389	.268	78.7	311	211	607	.425
72.3	168	067	452	.449	78.8	377	277	674	.617
72.4	232	131	516	.632	78.9	443	343	740	.809
72.5	295	194	579	.814	79.0	1.40509	1.40409	1.40806	111.002
72.6	359	258	643	.997	79.1	575	475	872	.195
72.7	423	322	707	99.179	79.2	641	541	938	.388
72.8	486	385	771	.362	79.3	707	607	1.41005	.581
72.9	550	450	836	.545	79.4	774	674	072	.775
73.0	1.36614	1.36514	1.36900	99.728	79.5	840	740	138	.968
73.1	678	578	964	.912	79.6	906	806	204	112.161
73.2	742	642	1.37028	100.095	79.7	972	872	270	.354
73.3	805	705	092	.278	79.8	1.41039	939	337	.549
73.4	869	769	156	.462	79.9	105	1.41005	404	.743
73.5	933	833	220	.646	80.0	1.41172	1.41072	1.41471	112.938
73.6	997	896	283	.827	80.1	238	138	537	113.131
73.7	1.37061	960	347	101.014	80.2	304	204	603	.326
73.8	125	1.37024	411	.198	80.3	371	271	670	.521
73.9	189	088	476	.383	80.4	437	337	737	.715
74.0	1.37254	1.37153	1.37541	101.568	80.5	504	404	804	.911
74.1	318	217	605	.753	80.6	571	472	872	114.106
74.2	382	281	669	.937	80.7	637	537	937	.301
74.3	446	345	733	102.122	80.8	704	604	1.42004	.497
74.4	511	410	798	.308	80.9	771	671	072	.692
74.5	575	475	864	.493	81.0	1.41837	1.41737	1.42138	114.888
74.6	639	539	928	.679	81.1	904	804	205	115.084
74.7	704	604	993	.865	81.2	971	871	272	.280
74.8	768	668	1.38057	103.050	81.3	1.42038	938	339	.477
74.9	833	733	122	.237	81.4	105	1.42005	906	.673
75.0	1.37897	1.37797	1.38187	103.423	81.5	172	072	474	.870
75.1	962	862	252	.609	81.6	239	139	541	116.067
75.2	1.38026	926	316	.796	81.7	306	206	608	.264
75.3	091	991	381	.983	81.8	373	273	675	.461
75.4	156	1.38055	445	104.170	81.9	440	340	742	.658

TABLE 2.—*Densities of pure sucrose solutions*—Continued

Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo	Brix or true per cent d. s. by weight	True density (Plato) 20°	Apparent density 20°	Apparent specific gravity 20°/20°	g sucrose per 100 ml weight in vacuo
1	2	3	4	5	1	2	3	4	5
82.0	1.42507	1.42407	1.42810	116.856	83.0	1.43181	1.43081	1.43486	118.84
82.1	574	475	878	117.053	83.1	248	148	553	119.03
82.2	642	543	946	.252	83.2	316	216	621	.22
82.3	709	609	1.43013	.449	83.3	383	283	688	.43
82.4	776	677	080	.647	83.4	451	351	756	.63
82.5	843	744	148	.845	83.5	519	419	824	.83
82.6	911	811	214	118.044	83.6	587	488	894	120.03
82.7	978	878	282	.243	83.7	654	555	961	.23
82.8	1.43046	946	350	.442	83.8	722	623	1.44029	.43
82.9	113	1.43013	417	.641	83.9	790	691	097	.64

WASHINGTON, December 19, 1932.

RP537

THERMOELECTRIC PROPERTIES OF PLATINUM-RHODIUM ALLOYS

By Frank R. Caldwell

ABSTRACT

The thermal electromotive forces and thermoelectric powers of a series of platinum-rhodium alloys against pure platinum have been determined from 0° to 1,200° C. The results obtained are compared with those obtained by other investigators.

The specimens used in this work contained the following percentages of rhodium, 0.100, 0.500, 1.000, 5.00, 21.6, 39.0, 51.6, 56.6, 61.2, 80.7, and 100.00.

CONTENTS

	Page
I. Introduction	373
II. Materials and methods used	374
III. Results	376
IV. Summary	380

I. INTRODUCTION

The thermoelectric properties of the series of platinum-rhodium alloys are of more than incidental interest. In the first place it has become an almost universal practice to express the thermoelectric properties of substances in terms of their thermal electromotive forces or thermoelectric powers against pure platinum. Secondly, the thermal electromotive force of the platinum versus 90 per cent platinum-10 per cent rhodium thermocouple serves to define the International Temperature Scale [1] in the range 660° to 1,063° C. Furthermore, platinum to platinum-rhodium thermocouples of higher rhodium content are frequently used in thermoelectric temperature measurements.

Several observers have reported measurements of the thermoelectromotive forces of the platinum-rhodium alloys against pure platinum. The principal data are those of Holborn and Wien, 1892,[2] for rhodium contents of 9,10, 11, 15, 20, 30, 40, and 100 per cent; Holborn and Day, 1899,[3] for pure rhodium; Day and Sosman, 1909,[4] for 10 and 20 per cent rhodium; Sosman, 1910,[5] for a series of alloys containing from 1 to 20 per cent rhodium; Waidner and Burgess, 1907,[6] for 10 and 20 per cent rhodium. In addition to the values determined by himself, Sosman [5] included a summary of the results of previous observers who had used the higher percentages of rhodium.

[1] G. K. Burgess, International Temperature Scale, B. S. Jour. Research, vol. 1, p. 635, 1928.
[2] Holborn and Wien, "Uber die Messung hoher Temperaturen," Annalen der Physik, vol. 47, pp. 107-134, 1892.
[3] Holborn and Day, Thermoelectricity in Certain Metals, Am. J. Sci. (4), vol. 8, pp. 303-308, 1899.
[4] Day and Sosman, The Nitrogen Thermometer from Zinc to Palladium, Am. J. Sci (4), vol. 29, p. 119, 1910.
[5] Sosman, The Platinum-Rhodium Thermoelement, Am. J. Sci. (4), vol. 30, p. 1, 1910.
[6] Waidner and Burgess, The Melting Points of Palladium and Platinum, B. S. Bull., vol. 3, p. 200, 1907.

The values given by him have been used for comparison between the values given later in this paper and those of other observers.

In 1914 Adams [7] published a table giving the corresponding values of temperature and thermal electromotive force for the 90 per cent platinum-10 per cent rhodium alloy against platinum. This table has served for nearly 20 years as the standard of reference for this type of thermocouple.

While in some cases there is good agreement between the values obtained by different observers, such seems to be the exception rather than the rule. Accordingly, when rhodium and platinum-rhodium alloys of exceptionally high purity were produced in the course of the work on the purification of the platinum metals at the Bureau of Standards, it appeared desirable to redetermine the thermoelectric properties of these materials.

II. MATERIALS AND METHODS USED

Eleven alloys were used in this work, the rhodium contents as determined by analysis being 0.100, 0.500, 1.000, 5.00, 21.6, 39.0, 51.6, 56.6, 61.2, 80.7, and 100.00 per cent. There seemed to be no reason for determining the thermal electromotive force of a particular sample of a 10 per cent rhodium alloy prepared expressly for this work, since a wealth of data on this alloy has been collected at the Bureau of Standards as a result of years of routine calibrations of standard thermocouples. The values given for the 10 per cent rhodium alloy are very close to the values to be found in the table prepared by Adams.[8]

A platinum-10 per cent rhodium thermocouple, designated as D-3 was used for temperature determinations. This thermocouple was calibrated at the freezing points of gold, silver, and antimony in accordance with the International Temperature Scale,[9] and in addition at the freezing points of zinc, lead, and tin and the boiling point of water in order to extend its range to 0° C. The thermal electromotive forces of the alloys against the platinum element of D-3 were measured and corrections applied for the differences between this platinum and the sample of spectroscopically pure platinum used at the Bureau of Standards as the standard of purity.

In this connection it may be pointed out that the thermoelectric properties of a sample of platinum are a more sensitive indication of purity than even spectroscopic tests. The smallest amount of impurity which has been detected spectroscopically in platinum corresponds to a change in the thermal electromotive force of about 20 μv at 1,200° C. In some cases, depending upon the impurities present, the thermal electromotive force against the standard platinum has been found to be as much as 50 μv at 1,200° C., when spectroscopic tests failed to show any impurity.

In general, small amount of impurities usually found in platinum make it positive thermoelectrically to pure platinum. Every sample of platinum ever tested thermoelectrically at the Bureau of Standards, with one exception, has been found to be positive to Pt 27, the

[7] Adams, Calibration Tables for Copper-Constantan and Platinum-Platinrhodium Thermoelements, J. Am. Chem. Soc., vol. 36, p. 65, 1914. Interna. Critical Tables, vol. 1, p. 57, 1926. B. S. Tech. Paper, No. 170, p. 308, 1921.

[8] See footnote 7.

[9] See footnote 1, p. 373.

platinum standard of this bureau. This exception was a particular sample which was negative to the standard by only 2 μv at 1,200° C. For all practical purposes such a difference may be disregarded, and the two samples have been considered to be of equal purity. The platinum produced for thermocouples at the Bureau of Standards runs consistently purer than 0.99999; and it is probable that Pt 27, selected from this material for its exceptionally high purity, contains less than 1 part in 10^6 of impurity.

The method used in obtaining the values of thermal electromotive force of the alloy versus the platinum of thermocouple D–3 is similar to that used in the routine calibrations of thermocouples. Each alloy wire was heated electrically to about 1,500° C. and was held at this temperature for a few minutes after which it was fused to the hot junction of thermocouple D–3.

The thermocouple and alloy wires, in suitable insulating and protection tubes, were inserted in a chromel tube furnace whose temperature may be varied by small steps over the range from room temperature to 1,200° C. The thermocouple was connected to one potentiometer, and the platinum element of the thermocouple and the alloy wire were connected to another, each potentiometer having its own reflecting galvonometer. The connections were made through a cold junction bottle maintained at 0° C. The two lines of light from the galvanometers were thrown on the same scale, the galvanometers and light sources being so adjusted that on open circuit both lines of light came to rest on zero. The potentiometer connected to the standard thermocouple was set on the value of electromotive force corresponding to 50° C. and the temperature of the furnace was slowly increased. While the temperature was rising, the two lines of light on the scale were made to coincide as they crossed the zero of the scale by manipulation of the slide wire of the potentiometer connected to the alloy wire and platinum element of D–3. The potentiometer reading at this instant gave the electromotive force of the alloy against the platinum of the standard thermocouple at 50° C. This process was repeated at temperature intervals of 50° up to 1,150° C. The temperature of the furnace was then slowly reduced, and similar observations made. The means of the values obtained with increasing and decreasing temperatures were used and values at 1,200° C. were obtained by extrapolation.

The thermal electromotive force of the platinum wire of D–3 versus the platinum standard Pt 27 was determined several times during the series of determinations in the same manner. These values were added to those obtained for the alloy versus the platinum of D–3 to obtain the thermal electromotive force against Pt 27.

The furnace used consists of a chromel tube about 53 cm long, open at both ends, clamped between two water-cooled terminals. This tube is in the secondary circuit of a transformer whose primary voltage can be varied from 11 to 220 volts in steps of 11 volts. The temperature gradients at the ends of the tube are sharp, and the temperature is sensibly uniform over the middle portion of the tube. This uniform temperature distribution and sharp gradient make it possible to test the homogeneity of the materials by changing the depth of immersion of the thermocouple and alloy in the furnace. Measurements on all alloys used were made at several depths of immersion without detecting any inhomogeneity.

III. RESULTS

The results of measurements on the alloys actually used are given in Tables 1 and 2. Curves, shown in Figure 1 have been drawn from the data in these tables. Table 3, the data in which were obtained from these curves, will probably be found more convenient for interpolation than Table 2. The values of Tables 1 and 3 are plotted in Figure 2. The thermoelectric powers obtained from the values of Tables 1 and 3 are plotted as functions of temperature in Figure 3.

The observations at a given temperature taken with increasing and decreasing temperature in no case differed by more than 6μv, and in general the difference ranged from 0 to 3μv. The mean of these two values at a given temperature never differed more than 3μv from the

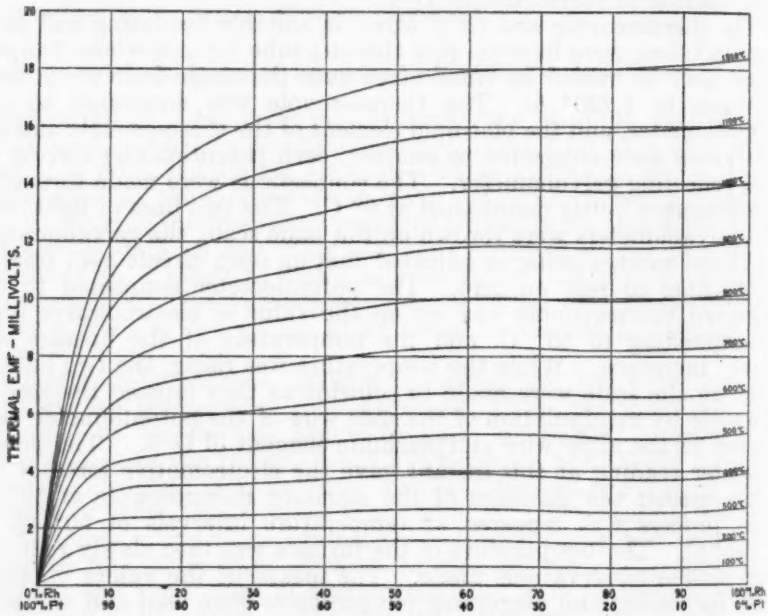


FIGURE 1.—*Thermal electromotive force of platinum-rhodium alloys against platinum plotted against composition*

corresponding means obtained at different times and at different depths of immersion. The values reported are given in terms of the international volt and include potentiometer corrections and the correction to convert the actual observations to thermal electromotive forces versus Pt 27.

While it is believed that the measurements of electromotive force are accurate to about 3μv, the tabulated results expressing electromotive force as a function of composition can not be considered as accurate as this at the higher temperatures on account of uncertainties in chemical analyses. For the analyses given, the values at the higher temperatures are not considered accurate to better than 5μv for the 0.1 and 0.5 per cent rhodium 10μv for the 1 and 100 per cent rhodium, 40μv for the 20 per cent rhodium and 20μv for the other alloys.

TABLE 1.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum for compositions containing 0.1 to 10.0 per cent rhodium*

Temperature	Per cent rhodium				
	0.1	0.5	1.0	5.0	10.0
° C.					
50	+0.009	+0.049	+0.088	+0.255	+0.298
100	.020	.097	.180	.536	.643
150	.031	.146	.275	.837	1.025
200	.042	.195	.372	1.154	1.436
250	.053	.245	.471	1.479	1.867
300	.065	.294	.568	1.809	2.315
350	.076	.343	.663	2.143	2.777
400	.087	.391	.758	2.479	3.249
450	.098	.438	.852	2.816	3.730
500	.109	.484	.945	3.155	4.218
550	.119	.530	1.037	3.494	4.715
600	.130	.576	1.128	3.835	5.221
650	.140	.621	1.219	4.177	5.737
700	.150	.666	1.309	4.520	6.260
750	.161	.711	1.398	4.866	6.791
800	.171	.756	1.489	5.216	7.331
850	.181	.802	1.579	5.569	7.879
900	.192	.847	1.669	5.924	8.435
950	.202	.892	1.760	6.282	8.998
1,000	.213	.937	1.852	6.643	9.570
1,050	.223	.982	1.943	7.007	10.149
1,100	.233	1.028	2.034	7.375	10.737
1,150	.244	1.073	2.126	7.746	11.329
1,200	.254	1.118	2.218	8.121	11.922

TABLE 2.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum for compositions containing 20 to 100 per cent rhodium*

Temperature	Per cent rhodium						
	21.6	39.0	51.6	56.6	61.2	80.7	100.0
° C.							
50	+0.280	+0.295	+0.306	+0.304	+0.298	+0.276	+0.314
100	.620	.651	.682	.676	.672	.623	.696
150	1.010	1.060	1.115	1.109	1.105	1.028	1.127
200	1.443	1.515	1.596	1.592	1.590	1.492	1.606
250	1.913	2.011	2.119	2.120	2.120	2.002	2.128
300	2.415	2.543	2.678	2.685	2.687	2.554	2.687
350	2.945	3.107	3.268	3.286	3.288	3.144	3.282
400	3.500	3.700	3.888	3.914	3.920	3.770	3.915
450	4.077	4.322	4.537	4.577	4.582	4.430	4.580
500	4.675	4.972	5.215	5.266	5.275	5.122	5.281
550	5.294	5.650	5.922	5.982	5.997	5.846	6.010
600	5.936	6.356	6.657	6.732	6.747	6.602	6.772
650	6.599	7.085	7.419	7.505	7.525	7.389	7.566
700	7.282	7.847	8.207	8.307	8.331	8.206	8.398
750	7.984	8.633	9.024	9.134	9.165	9.053	9.262
800	8.702	9.446	9.869	9.996	10.028	9.931	10.158
850	9.443	10.286	10.742	10.885	10.922	10.839	11.085
900	10.201	11.152	11.645	11.797	11.844	11.777	12.043
950	10.977	12.043	12.577	12.741	12.795	12.746	13.034
1,000	11.771	12.960	13.538	13.714	13.776	13.745	14.050
1,050	12.582	13.902	14.526	14.711	14.785	14.773	15.100
1,100	13.411	14.870	15.540	15.737	15.822	15.830	16.181
1,150	14.257	15.862	16.580	16.787	16.890	16.914	17.292
1,200	15.121	16.876	17.646	17.863	17.986	18.024	18.432

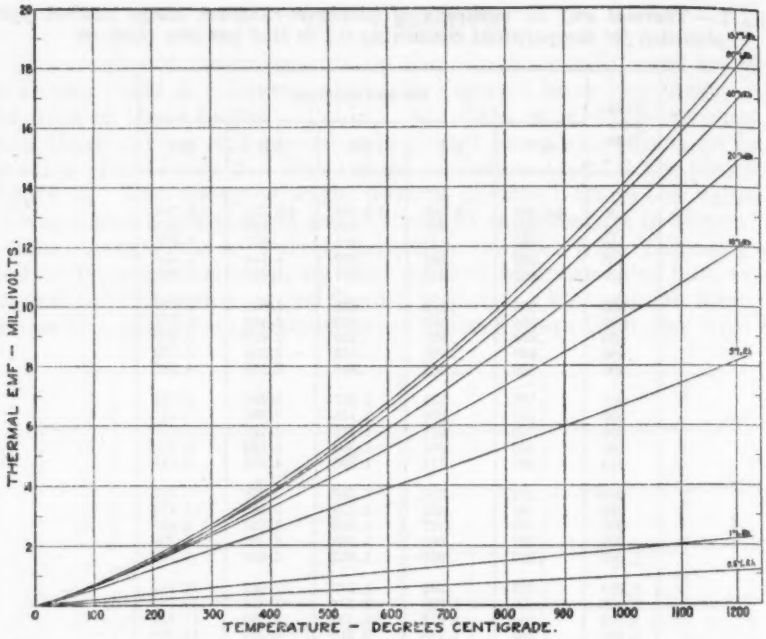


FIGURE 2.—*Thermal electromotive force of platinum-rhodium alloys against platinum plotted against temperature*

TABLE 3.—*Thermal emf in millivolts of platinum-rhodium alloys against pure platinum, adjusted values*

Temperature	Per cent rhodium						
	20.0	40.0	50.0	55.0	60.0	80.0	100.0
° C.							
100	+0.63	+0.65	+0.68	+0.68	+0.67	+0.62	+0.70
200	1.44	1.52	1.59	1.59	1.59	1.49	1.61
300	2.40	2.55	2.67	2.69	2.68	2.55	2.68
400	3.47	3.70	3.87	3.90	3.92	3.77	3.91
500	4.63	4.97	5.19	5.24	5.27	5.12	5.28
600	5.87	6.36	6.62	6.70	6.74	6.60	6.77
700	7.20	7.85	8.17	8.27	8.32	8.20	8.40
800	8.59	9.45	9.82	9.95	10.02	9.92	10.16
900	10.06	11.16	11.59	11.75	11.83	11.76	12.04
1,000	11.58	12.98	13.47	13.65	13.76	13.73	14.05
1,100	13.17	14.90	15.46	15.66	15.80	15.81	16.18
1,200	14.84	16.91	17.56	17.79	17.94	17.99	18.42

From the values given in Table 1 it can be seen that the thermal electromotive force does not always increase with rhodium content, and that some of the curves of Figure 2, obtained by adjusting the values of Tables 1 and 2 for even percentages cross at the lower temperatures. This result agrees in general with the determinations of previous observers.

Referring to Figure 1, it will be noted that the curves exhibit fairly definite maxima in the region of 60 per cent rhodium. Since the alloy containing 56.6 per cent rhodium was the only one in the original group whose rhodium content was within the range 40 to 80 per cent,

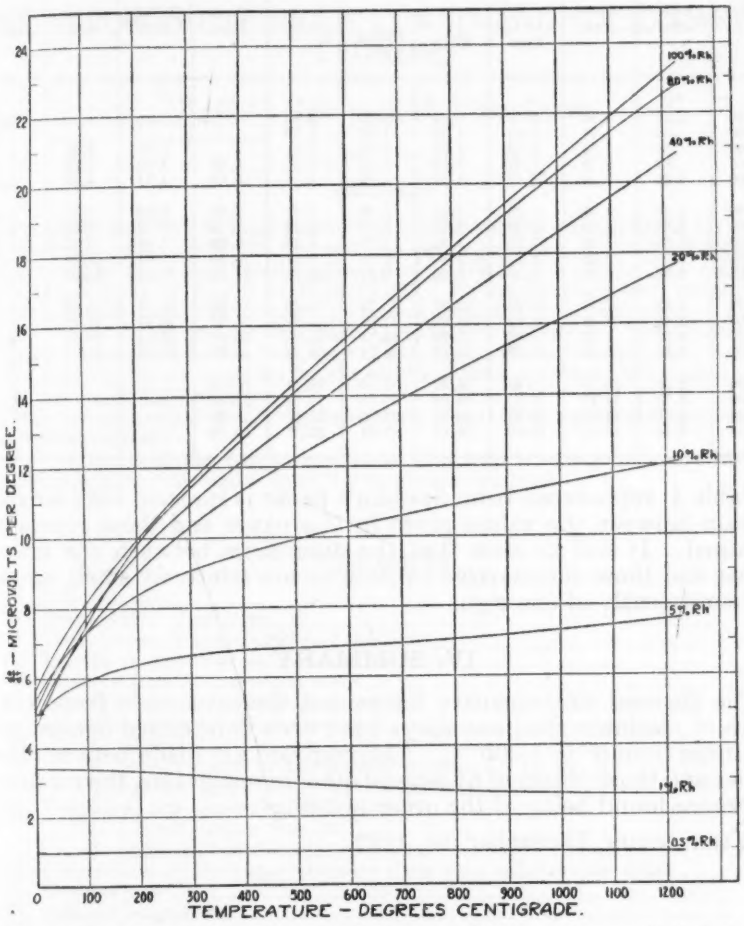


FIGURE 3.—*Thermoelectric power of platinum-rhodium alloys against platinum plotted against temperature*

it was thought desirable to check the data obtained with this alloy. This was done by preparing two additional alloys containing 51.6 and 61.2 per cent rhodium. The data obtained with these additional alloys confirmed the data previously obtained with the 56.6 per cent rhodium alloy.

TABLE 4.—*Thermal emf of pure platinum against platinum-rhodium alloys, in millivolts*

[Reproduced from Sosman's paper]

t	1 per cent	5 per cent	10 per cent			15 per cent	20 per cent	30 per cent	40 per cent	100 per cent
			Low	High	Standard					
	°C.									
100	0.21	0.55	0.63	0.64	0.64	0.65	----	----	----	0.65
200	.42	1.18	1.41	1.43	1.43	1.50	----	----	----	1.51
300	.63	1.85	2.28	2.32	2.32	2.41	----	2.34	2.45	2.57
400	.84	2.53	3.21	3.26	3.25	3.45	3.50	3.50	3.64	3.76
500	1.05	3.22	4.17	4.23	4.23	4.55	4.60	4.74	4.93	5.08
600	1.25	3.92	5.16	5.24	5.23	5.71	5.83	6.06	6.31	6.55
700	1.45	4.62	6.19	6.28	6.27	6.94	7.18	7.49	7.80	8.14
800	1.65	5.33	7.25	7.35	7.33	8.23	8.60	9.01	9.37	9.87
900	1.85	6.05	8.35	8.46	8.43	9.57	10.09	10.67	11.09	11.74
1,000	2.05	6.79	9.47	9.60	9.57	10.96	11.65	12.42	12.94	13.74
1,100	2.25	7.53	10.64	10.77	10.74	12.40	13.29	14.33	14.99	15.87
1,200	2.45	8.29	11.82	11.97	11.93	13.87	14.96	16.39	17.13	18.10
1,300	2.65	9.06	13.02	13.18	13.13	15.38	16.65	18.51	19.51	20.46
1,400	2.86	9.82	14.22	14.39	14.34	16.89	18.39	20.67	21.73	----
1,500	3.06	10.56	15.43	15.61	15.55	18.41	20.15	----	----	----
1,600	3.26	11.31	16.63	16.82	16.75	19.94	21.90	----	----	----
1,700	3.46	12.05	17.83	18.03	17.95	21.47	23.65	----	----	----
1,755	3.56	12.44	18.49	18.70	18.61	22.31	24.55	----	----	----

Table 4, reproduced from Sosman's paper is inserted here for comparison between the values given in this paper and those previously obtained. It will be seen that the differences between the present values and those summarized by Sosman are relatively small, and are not consistently of one sign.

IV. SUMMARY

The thermal electromotive forces and thermoelectric powers of a series of platinum-rhodium alloys have been determined against pure platinum from 0° to 1,200° C. Comparisons are made between these values and those obtained by several other investigators, the maximum difference found being of the order of 300 μv.

WASHINGTON, December, 14, 1932.

RP538

THE VAPOR PRESSURE OF LIQUID AND SOLID CARBON DIOXIDE

By C. H. Meyers and M. S. Van Dusen

ABSTRACT

The vapor pressure of liquid carbon dioxide from the critical point (31.0° C.) to the triple point (−56.60° C.) and the vapor pressure of the solid from the triple point to the normal sublimation point (−78.515° C.) have been measured with an accuracy of 1 or 2 parts in 10,000. Equations have been obtained to represent these data, the average deviations from the equations being 1 part in 10,000 for the liquid and about 2 parts in 10,000 for the solid. The equation for the solid represents also the best work of other laboratories at and below −78° C.

The vapor-pressure equation for the solid has been correlated with calorimetric data from other laboratories.

Pressures and relative volumes have been observed along several isotherms in the critical region.

A set of tables of the vapor pressure and the rate of change of vapor pressure with temperature calculated from the equations are given.

CONTENTS

		Page
I.	Introduction	381
II.	Preparation of samples	382
III.	Description of apparatus and method	383
IV.	Results of vapor-pressure measurements	385
V.	Observations at the triple point	388
VI.	Observations at the critical point	389
VII.	Measurements by other observers	392
	1. Observations at the triple point	392
	2. Observations at the critical point	392
	3. Review of vapor-pressure measurements	394
VIII.	Empirical representation of the data	399
	1. Liquid carbon dioxide	399
	2. Solid carbon dioxide	402
IX.	Correlation of the vapor-pressure data with calorimetric data	404
X.	Conclusions	407
XI.	Acknowledgments	408
XII.	Appendix	408

I. INTRODUCTION

The determination of the vapor pressure is one of a series of investigations on the thermodynamic properties of refrigerants conducted at the Bureau of Standards.

The measurements consisted of three sets made at different times. In 1919 and 1920 observations were made covering the range −55° to +31° C. The results of these observations were published [1] in 1926. These results have been recalculated and will be presented here together with the more recent observations.

[1] Ref. Eng., vol. 13, p. 180, 1926.

In 1927 one of the original samples of CO_2 (used in the first series) was sent to the Massachusetts Institute of Technology where its vapor pressure at 0° C. was measured. In 1929 the vapor pressure of the same sample at 0° C. and at 25° C. was measured at this bureau.

In 1931 the vapor pressure of another of the original samples was measured in the range −50° to −79° C. No measurements below −79° C. have been made in the course of the work, but the published data have been reviewed critically and used in deriving an empirical equation for the vapor pressure of the solid over a wide temperature range.

II. PREPARATION OF SAMPLES

The liquid carbon dioxide used in these measurements was prepared by C. S. Taylor, formerly of the chemistry division of this bureau. Sodium bicarbonate and concentrated sulphuric acid which

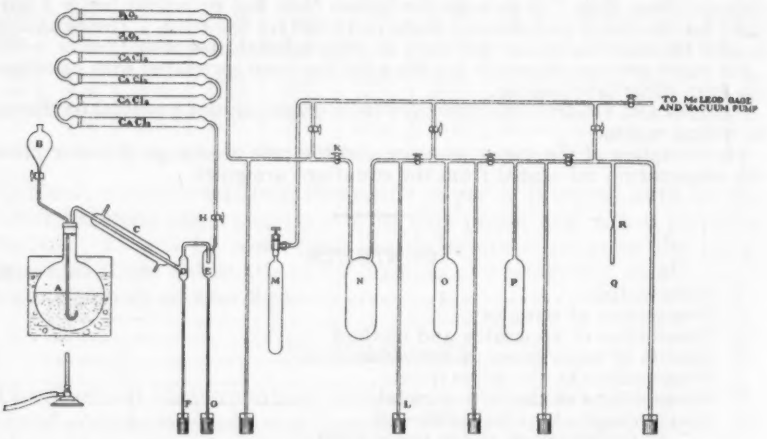


FIGURE 1.—*Apparatus for preparing samples*

had been heated in order to expel traces of air were used for this purpose. The generating apparatus was very similar to that used and described by Bradley and Hale.[1] The flask *A* (fig. 1) was about half filled with sodium bicarbonate and sufficient distilled water was then added to form a thin paste. A dropping funnel *B* with its tip turned upward and a gas delivery tube were introduced through a rubber stopper which sealed the flask. The dropping funnel contained concentrated sulphuric acid, freshly boiled and cooled. The delivery tube was connected with the condenser *C*, traps, and drying train.

The entire apparatus was evacuated to the vapor pressure of water, the flask was heated to approximately 100° C. by means of a water bath, and sulphuric acid admitted slowly into the flask. The flask and line were purged by discharging some carbon dioxide through the mercury seals *F* and *G* of traps *D* and *E*. Condensed water was also discharged through these mercury seals. After the entire system had been purged several times, the gas was allowed to flow through a

[1] J. Am. Chem. Soc., vol. 30, 1090, 1908.

drying train containing $CaCl_2$ and sublimed P_2O_5, and finally frozen into bulb *N* by cooling with liquid air. When sufficient quantity of carbon dioxide had been collected in *N*, stopcock *K* was closed and the bulb connected to the vacuum pump, so that any gas not occluded in the crystals would be pumped out. The liquid air bath was then transferred to container *O* and after bulb *N* had warmed sufficiently so that gas was escaping freely through the mercury at *L*, the carbon dioxide was sublimed into container *O*. Gas not occluded in the crystals was then pumped out as before. The carbon dioxide was then distilled into a glass high-pressure container *M* fitted with a steel valve fastened to the glass by a method described elsewhere.[3]

After the carbon dioxide had warmed up and liquefied, the valve was opened slightly and the gas allowed to escape so rapidly that the remaining liquid was frozen by its own evaporation. The valve was then closed until liquid formed and the process repeated several times. The carbon dioxide was next sublimed into bulb *P*, the first and last portions being rejected. Then, as before, any gas not occluded in the crystals was pumped out. The carbon dioxide was sublimed back and forth between *O* and *P* eight times in all, and then sublimed into the apparatus sealed on at *Q*. While *Q* was still cooled with liquid air the vacuum pump was connected to it, and the apparatus sealed off at *R* by fusion.

As a test for purity 1,000 ml of the purified gas was dissolved in potassium-hydroxide solution in a pipette. From the fact that the residual bubble was microscopic and also from observations of the pressure when the sample was at liquid air temperature, together with a knowledge of the capacity of the sample container, it was estimated that the carbon dioxide contained less than 1 part in 1,000,000 by volume of noncondensing impurities.

III. DESCRIPTION OF APPARATUS AND METHOD

The samples used in this investigation were contained in three types of containers illustrated in Figure 2. Each of the containers of type 1 consisted of a glass U tube about 2.5 mm inside diameter, to which a valve was soldered.[4] These samples of carbon dioxide could be totally immersed in the constant temperature bath. Of the two such containers filled in 1919, one sample (designated by No. 1) is still intact (1932), the other (No. 2) failed by leakage through a soldered joint after one day of observations.

One container of type 3 was used. It consists of a glass bulb connected through glass tubing to a manometer (about 8 mm inside diameter and 1 m long) which was similarly soldered to a valve. During the observations the pressure was transmitted from the manometer on the container of this sample to the pressure gauge by an air pressure approximately equal to the carbon dioxide pressure. For the observations made in 1931 the constancy of this transmitting pressure was improved by attaching a container of about 1 liter capacity to the line and immersing the container in an ice bath. In order to avoid pressures which might rupture the glass when the sample

[3] McKelvy and Taylor, J. Am. Chem. Soc., vol. 42, p. 1364, 1920. Meyers, J. Am. Chem. Soc., vol. 45, p. 2135, 1923.
[4] See footnote 3.

was at room temperature, the amount of carbon dioxide used wa sufficient only to produce liquid at temperatures below −20° C.

The containers of type A were of steel tinned inside and out.

The pressures were measured with dead-weight pressure gauge which are sensitive to better than 1 part in 10,000. These gauges together with the calibration and method of use have been describe in a previous paper.[5]

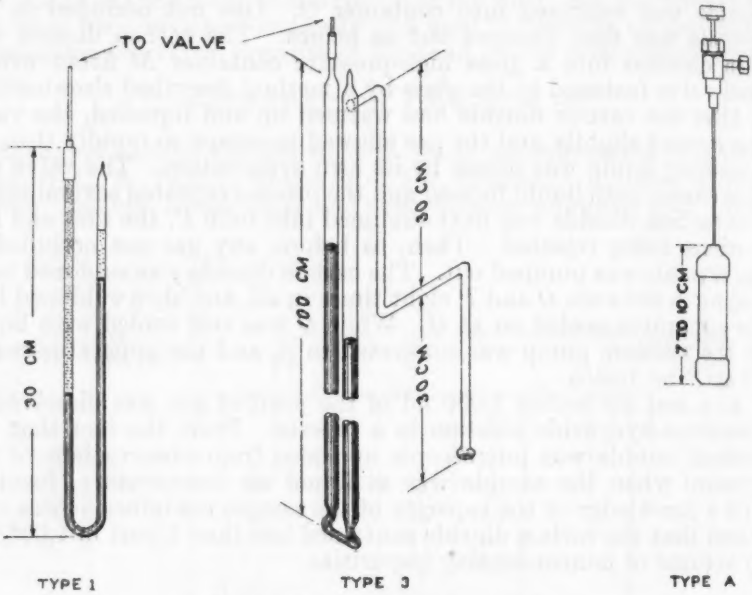


FIGURE 2.—*Containers for samples*

Temperatures were observed with platinum-resistance thermometers of the 4-lead potential terminal type, with strain-free windings inclosed in a tube.[6]

The Wheatstone bridges used both in the earlier observations[7] and in those[8] of 1931 have also been described in previous papers.

During the vapor-pressure measurements the carbon dioxide was maintained at a constant and uniform temperature in one of a number of stirred thermoregulated baths, the one chosen being determined by the temperature and the type of carbon-dioxide container. During the earlier observations the thermometer inserted near the carbon dioxide sample indicated no changes greater than 0.005° C. for periods of 20 minutes to 2 hours before the observation. The temperature differences between various parts of the baths were of the same order of magnitude. Some of the observations at 0° C. were made with the sample in an ice bath. The observations in 1931 were made with a bath[9] which could be controlled for a long time within 0.001° or 0.002° C. and which showed equally uniform temperature from place to place in the bath.

[5] B. S. Jour. Research, vol. 6 (R. P. 324), p. 1061, 1931.
[6] B. S. Bull., vol. 6 (S124), p, 154, 1910. B. S. Sci. Papers, vol. 17 (S407), p. 49, 1922.
[7] B. S. Bull., vol. 11 (S241), p. 571, 1915.
[8] B. S. Bull., vol. 13 (S288), p. 547, 1917.
[9] B. S. Jour. Research, vol. 6 (RP284), p. 401, 1931.

To obtain correct results with the static method used, it is necessary that there be no temperature difference between the liquid or solid surface of the sample and the thermometer, a condition which can occur only when no condensation or evaporation is taking place. In order to reduce to a minimum the time required to attain such equilibrium within the sample, the apparatus was manipulated in such a way that equilibrium was reached through condensation of a portion of the sample. This precaution was found to be even more necessary for the solid than for the liquid, since the solid sometimes broke loose from the container and in consequence was in very poor thermal contact with its surroundings. Attainment of equilibrium has been discussed in detail in connection with the vapor pressure measurements of ammonia.[10]

IV. RESULTS OF VAPOR-PRESSURE MEASUREMENTS

The results of the observations on the vapor pressure of liquid carbon dioxide are given in Table 1. All the pressure measurements have been reduced to millimeters of mercury at 0° C. and at standard gravity ($g = 980.665$). The value of g (980.091) assumed for this laboratory is based on a determination made by the United States Coast and Geodetic Survey in 1910.[11] The thermometers have been calibrated in accordance with the specifications for the international temperature scale.[12]

The results obtained with samples in metal containers (Type A) and previously published [13] were given no weight in selecting the final values and have been omitted, because the conditions of observation were not conducive to accurate results, namely, (1) leaks in the valve packings were found at numerous times, and small leaks sufficient to lower the observed vapor pressure probably occurred undetected at other times; (2) the carbon dioxide may have acquired impurities in the connection between the metal container and the pressure gage, such as air not completely washed out of the tubing or wax dissolved from the valve packings.

In numerous cases the previously published data represented the mean of several readings which may be considered as separate observations, even though made successively at the same temperature, since for each reading the sample occupied a somewhat different volume. The values of temperature and pressure for these separate observations have been recalculated and are given in columns 3 and 4, respectively. A general increase of about 1 part in 5,000 over the previously published values of pressure is thus obtained.

Not all the measurements recorded can be considered as having the same weight. In some cases the greater number of readings and longer period of time covered insured that there was no drift in the observed values, and on some days the thermostat in the bath was operating better than on other days. Lack of space prevents the presentation of all these details for the reader's judgment in the matter, but in the review of the data an estimate was attempted of the relative merits

[10] B. S. Bull., vol. 16 (S369), p. 1, 1920. Am. Soc. Ref. Eng. J., vol. 6, p. 307, 1920.
[11] B. S. Bull., vol. 8 (S171), p. 363, 1911.
[12] B. S. Jour. Research, vol 1 (R. P. 22), p. 635, 1928.
[13] See footnote 1, p. 381.

of the observations. This estimate is recorded in column 5 of Table 1 where the number indicates the weight to be given to the observation when an average value is to be taken. It is believed that the values thus weighted yield slightly more probable averages than would be obtained from equally weighted observations. The values calculated from an equation (column 6, discussed in Sec. VIII of this paper) were not considered in making this estimate.

The measurements in July, 1920, were made with special attention toward securing thermal equilibrium, the bath temperature being maintained constant within 0.005° C. for two or three hours at each of the temperatures 20°, 25°, 30°, and 31° C. Observations were made at −5° C. during the same month, but the pressure readings were erratic due evidently to partial freezing of the oil in the manometer. The trouble was so apparent that the data have been omitted. It is possible that the observation taken at 0° C. during the same month may also be slightly in error due to the same cause. This source of error has been avoided in all later measurements by substituting an oil with a lower pour point.

The accuracy of the observations taken in 1929 at 25° C. is impaired by a tendency of the bath temperature to drift. Although the temperature was kept constant within 0.005° C. by manual correction of this tendency, the observations should be given less weight than other observations.

The temperature of the bath used in 1931 for the range −50° to −79° C. was remarkably constant (0.001° or 0.002° C.), but the accuracy of the observations in March of that year was limited by uncertainty in observing the mercury surface in a manometer attached to the piston gage. The observations in April are more reliable, since they were made after removing the mercury from the manometer in question and allowing the transmitting air pressure to come directly in contact with the oil in the manometer. In addition, more care was taken to insure attainment of equilibrium.

TABLE 1.—*Measurements of the vapor pressure of liquid carbon dioxide*

Date	Sample No.	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated—		
						Pressure		Temperature
		°C.	mm		mm	mm	*Parts in 100,000*	*0.001°C.*
June 2, 1920	3	−50.002	5,127.6	1	5,127.5	0.1	2	0
	3	−49.966	5,134.8	1	5,134.9	−.1	−2	0
	3	−45.011	6,246.8	1	6,247.2	−.4	−6	1
	3	−44.994	6,250.9	1	6,251.2	−.3	−5	1
	3	−44.982	6,253.3	1	6,254.2	−.9	−15	4
	3	−44.981	6,257.1	1	6,254.4	2.7	43	−11
May 29, 1920	3	−40.005	7,543.6	1	7,543.6	0	0	0
	3	−39.971	7,555.1	1	7,553.0	2.1	28	−8
May 28, 1920	3	−35.002	9,028.6	4	9,028.4	.2	2	−1
	3	−34.998	9,031.7	1	9,029.7	2.0	22	−6
	3	−34.996	9,029.9	1	9,030.3	−.4	−4	1
	3	−34.988	9,032.6	1	9,032.9	−.3	−3	1
	3	−30.005	10,716.8	1	10,716.7	.1	1	0
	3	−29.988	10,722.3	4	10,722.8	−.5	−5	1
	3	−29.982	10,722.1	1	10,725.0	−2.9	−29	8

TABLE 1.—*Measurements of the vapor pressure of liquid carbon dioxide*—Contd.

Date	Sample No.	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated— Pressure		Temperature
		°C.	mm		mm	mm	Parts in 100,000	0.001°C.
July 21, 1920	1	−.003	26,134.1	1	26,139.5	−5.4	−21	8
July 15, 1920	1	5.001	29,771.4	1	29,771.7	−.3	−1	0
July 17, 1920	1	5.003	29,774.3	1	29,773.3	1.0	3	−1
	1	9.995	33,759.4	4	33,759.1	.3	1	0
July 16, 1920	1	15.000	38,148.9	1	38,146.1	2.8	7	−3
July 16, 1920	1	15.000	38,147.5	4	38,146.1	1.4	4	−2
July 14, 1920	1	19.999	42,961	4	42,958	3	8	−3
	1	20.000	42,960	2	42,959	1	3	−1
July 13, 1920	1	24.998	48,247	2	48,247	0	0	0
July 13, 1920	1	24.999	48,250	2	48,248	2	5	−2
	1	25.001	48,248	4	48,251	−3	−6	3
May 13, 1920	1	29.986	54,054	1	54,069	−15	−28	12
May 12, 1920	1	29.987	54,060	1	54,070	−10	−18	8
May 13, 1920	1	29.988	54,058	4	54,071	−13	−24	10
May 12, 1920	1	29.990	54,061	1	54,074	−13	−24	10
	1	29.992	54,055	1	54,076	−21	−39	17
July 19, 1920	1	29.992	54,072	2	54,076	−4	−7	3
	1	29.993	54,073	4	54,078	−5	−9	4
May 12, 1920	1	29.995	54,074	2	54,080	−6	−11	5
May 11, 1920	1	30.021	54,099	1	54,112	−13	−24	10
May 18, 1920	1	30.799	55,078	2	55,076	2	4	−2
May 15, 1920	1	30.950	55,274	1	55,266	8	15	−7
May 13, 1920	1	30.988	55,316	1	55,312	4	7	−3
	1	30.989	55,319	1	55,313	6	11	−5
May 14, 1920	1	30.990	55,311	1	55,315	−4	−7	3
May 13, 1920	1	30.995	55,325	2	55,321	4	7	−3
	1	30.999	55,325	4	55,326	−1	−2	1
July 19, 1920	1	30.999	55,332	1	55,326	6	11	−5
	1	30.999	55,333	1	55,326	7	13	−6
May 15, 1920	1	31.003	55,344	1	55,331	13	24	−10
May 14, 1920	1	31.049	55,394	1	55,389	5	9	−4
May 17, 1920	1	31.050	55,391	1	55,390	1	2	−1
May 14, 1920	1	31.064	55,407	1	55,407	0	0	0
	1	31.069	55,412	1	55,414	−2	−4	2
May 19, 1920	2	31.081	55,440	1	55,429	11	20	−9
	2	31.081	55,436	1	55,429	7	13	−6
May 14, 1920	1	31.101	55,458	1	55,454	4	7	−3
Mar. 25, 1931	3	−56.476	3,905.4	1	3,906.5	−1.1	−28	6
Apr. 7, 1931	3	−56.434	3,913.4	4	3,913.6	−.2	−5	1
Mar. 24, 1931	3	−56.232	3,946.7	1	3,948.1	−1.4	−36	8
Apr. 6, 1931	3	−56.049	3,979.7	4	3,979.5	.2	5	−1
Mar. 24, 1931	3	−55.221	4,122.1	1	4,124.0	−1.9	−46	11
Mar. 26, 1931	3	−50.781	4,965.7	1	4,967.1	−1.4	−29	7
	3	−50.534	5,016.6	1	5,017.5	−.9	−18	4
Jan. 8, 1929	1	[1] 0	26,140.0	4	26,141.7	−1.7	−7	2
	1	[1] 0	26,139.9	4	26,141.7	−1.8	−7	3
Jan. 7, 1929	1	[1] 0	26,138.7	2	26,141.7	−3.0	−12	4
	1	[1] 0	26,139.0	4	26,141.7	−2.7	−10	4
Feb. 3, 1929	1	25.018	48,260	½	48,269	−9	−20	8
	1	25.026	48,269	½	48,278	−9	−18	8
	1	25.029	48,272	½	48,282	−10	−21	9
Jan. 31, 1929	1	25.116	48,378	½	48,378	0	0	0

[1] Observations on sample in ice bath.

All observations on the vapor pressure of the solid were made in 1931 on the one sample in a container of type 3. (Fig. 2.) The previous remarks in regard to the weighting and accuracy of observations on the liquid are applicable also to the solid. The results of these observations are given in Table 2 which is similar to Table 1.

TABLE 2.—*Measurements of the vapor pressure of solid carbon dioxide*

Date	Observed temperature	Observed pressure	Weight of observations	Calculated pressure	Observed minus calculated—		
					Pressure		Temperature
	°C.	mm		mm	mm	Parts in 100,000	0.001 °C.
Apr. 2, 1931	−78.797	[1] 742.44	4	742.57	−0.13	−17	2
	−78.796	742.53	2	742.63	−.10	−13	2
Mar. 24, 1931	−78.559	[1] 757.1	1	757.25	−.15	−20	2
	−78.551	757.9	1	757.73	.17	22	−3
Mar. 20, 1931	−78.506	[1] 760.5	1	760.53	−.03	−4	0
	−78.505	761.4	1	760.59	.8	105	−13
Apr. 3, 1931	−78.421	[1] 765.92	4	765.85	.07	9	−1
	−78.419	766.08	4	765.97	.11	13	−2
Mar. 20, 1931	−77.800	[2] 804.7	0	805.70	−1.0	−124	15
Mar. 25, 1931	−70.148	1,469.85	2	1,469.55	.35	24	−3
Mar. 24, 1931	−70.132	1,470.07	1	1,471.34	−1.27	−87	20
Mar. 20, 1931	−70.005	[2] 1,475.9	0	1,485.5	−9.6	−650	90
Apr. 2, 1931	−69.537	1,538.7	2	1,539.0	−.3	−20	3
Mar. 25, 1931	−60.265	3,017.2	1	3,016.7	.5	17	−2
Mar. 26, 1931	−60.222	3,024.8	2	3,025.8	−1.0	−33	4
Apr. 2, 1931	−60.134	3,044.74	2	3,044.4	.3	10	−1
		[3] 3,044.64					
Apr. 3, 1931	−59.851	3,104.46	2	3,105.2	−.8	−26	4
		[3] 3,104.39					
Mar. 25, 1931	−56.760	3,845.6	1	3,843.5	2.1	55	−8
Apr. 7, 1931	−56.655	3,871.94	2	3,871.1	.8	21	−3
		[3] 3,871.86					
Apr. 3, 1931	−56.653	3,871.00	4	3,871.6	−.7	−18	3
		[3] 3,870.80					
Apr. 6, 1931	−56.630	3,878.85	4	3,877.5	1.3	34	−5
		[3] 3,878.72					
Apr. 6, 1931	−56.629	3,878.69	2	3,877.8	0.8	21	−3
		[3] 3,878.56					

[1] This observation was made with the pressure gage disconnected and is therefore free from possible errors arising in the use of the piston gage, including the one mentioned in the following note.

[2] After the reading at −77.8 a leak from the container which held the transmitting air pressure was found. This observation is probably in error due to such leakage and no weight has been given to the result.

[3] This value was obtained with a 100-bar gage, the value immediately above was obtained with a 10-bar gage, the two gages being connected in parallel.

NOTE.—The uncertainty in reading the manometer on the sample container amounts to about 0.1 mm, but in some cases the values have been carried out to hundredths of a millimeter for purposes of comparison.

V. OBSERVATIONS AT THE TRIPLE POINT

All observations at the triple point were made on the one sample in the container of type 3. For the observations in 1920 of the pressure at the triple point, a glass tube about 7 cm in diameter closed at the lower end was partially immersed in a constant temperature bath at −52° C. The sample was lowered into the air space within this tube and sufficient carbon dioxide snow to freeze a portion of the sample was dropped into the tube. The liquid bath used in 1931 was under such excellent control that the sample was immersed directly in the bath. For the observations of April 7 the bath was adjusted to within a few hundredths of a degree of the triple point and observations

taken continuously over a period of 1 hour and 40 minutes. During this period there was a gradual rise in pressure within the limits given in Table 3, which contains the observations of the triple point pressure. This rise in pressure may be attributed to one or both of two possible causes, namely (1) a small amount of impurity in the sample, and (2) the solid may have been entirely covered by a film of liquid in which temperature gradients would be caused by heat transfer to or from the sample. In such case the vapor pressure would correspond to the temperature of the liquid-vapor surface and the rise in pressure would be explained by assuming that the temperature of this surface increased about 0.004° C. in consequence of the fact that the observer increased the bath temperature about 0.04° C. during the observations. If the variation in pressure is caused by soluble impurities, the larger value of pressure would be more nearly correct; if caused by variable temperature gradients, the smaller value would be more nearly correct.

The weighted mean of the values given in Table 3 is 3,885.27 mm. The vapor pressure equations for the liquid and for the solid, equations (6) and (9), respectively, in section VIII of this paper, intersect at about 3,885.10 mm and −56.602° C. These data indicate with fair certainty that the triple point pressure and temperature are, respectively, 3,885.2 ± 0.4 mm and −56.602 ± 0.005° C.

TABLE 3.—*Measurements of pressure at the triple point*

Date	Observed pressure		Weight of observation
	100-bar gage	10-bar gage	
	mm	*mm*	
June 3, 1920	3,884.1	----------	1
	3,886.9	----------	1
	3,885.4	----------	2
	3,886.1	----------	1
Apr. 6, 1931	3,885.05	3,885.09	2
	3,885.20	3,885.33	2
Apr. 7, 1931	3,884.68	3,884.77	2
	3,885.25	3,885.22	2

NOTE.—The uncertainty in reading the manometer on the sample container amounts to about 0.1 mm, but in some cases the values have been carried to hundredths of a millimeter for purposes of comparison.

VI. OBSERVATIONS AT THE CRITICAL POINT

Visual observations of the phenomena taking place in the sample at or near the critical point were made, but the critical temperature could not be fixed by this method much closer than about 0.1° C.

It may be noted that the critical point of a fluid is not a sharply defined point, such as the triple point, and can not be determined with the same degree of precision. No directly observable physical property exhibits a discontinuity at the critical point. The only discontinuities are those in the derivatives of certain quantities with respect to temperature or pressure, but such derivatives can not be directly observed. The exact critical temperature is therefore subject to considerable uncertainty, but the pressure-temperature relation in this region is definitely determinable. Near the critical point the compressibility of a fluid is very great, and appreciable differences in density therefore exist in a vertical column of the fluid. In this

manner the action of gravity affects the observed phenomena, and th value chosen for the critical temperature will depend to some exten upon the interpretation of the observations.

When the bath containing the sample was warmed at the rate o about 0.002° C. per minute the meniscus gradually became fainte and finally changed to a band about 1 or 2 mm wide which disappeare at 31.06° C. When the bath was cooled at the rate of about 0.006 per minute the band appeared at 31.02° C. When viewed wit reflected light a gray fog was visible in the band, and through th temperature range 31.05° to 31.15° C. this fog was faintly visibl throughout the sample.

In addition to these observations of the meniscus or band, the rela tive volumes occupied by samples Nos. 1 and 2 at various pressure were measured along several isotherms in the critical region. Fo these observations the sample was immersed in a bath maintained within a few thousandths of a degree centigrade of the constant temper ature desired. The carbon dioxide was first expanded until i existed as a superheated vapor. Then the weight on the piston gag was increased by small increments. After time had been allowe for attainment of equilibrium subsequent to each increase in weight the pressure and the length of the carbon dioxide column were ob served. At some of the temperatures the length of tube occupied by the carbon dioxide was also observed at the beginning and at the end of condensation.

The diameter of the tube was assumed constant except for the end which had been tapered in the sealing off process. This tapered end was assumed to be a cone and one-third of its length was added to the length of the portion of uniform diameter. The observed lengths of sample No. 2 had to be multiplied by the factor 1.075 to make them comparable with those of No. 1. Since the uncorrected length was usually measured with an accuracy of not better than one-half millimeter, errors of 1 or 2 per cent in the measurement of relative volume may be expected.

These measurements are represented in Figure 3 where the pressure is plotted as ordinate and the corrected length of tube as abscissa. It is apparent that the shape of the isotherms can not be used as a criterion for determining the critical temperature within 0.2° or 0.3° C.

It was at first thought that since the temperature of disappearance of the band depended to some extent upon the illumination, the mean of the temperatures for disappearance and appearance of the band, 31.04° C., was at or slightly below the critical temperature. The observations of Kennedy and Meyers [14] on the same sample in which the meniscus was observed to be a sharply defined surface up to about 30.96° C. and to be a band of finite width above this temperature, as well as their observations on samples in capillary tubes, and further consideration of the matter leads to the belief that the critical temperature is very near 30.96° C.

It is believed that the band observed above this temperature is due to the rapid change of density and optical properties with pressure for the single phase which is enormously compressible in the

[14] Ref. Eng., vol 15, p. 125, 1928.

critical region, and that this band would not be present if the sample were not in a gravitational field. Probably even a few hundredths of a degree below the critical temperature, the density of both the liquid and vapor at an infinitesimal distance from the meniscus differs appreciably from that in the remainder of the sample.

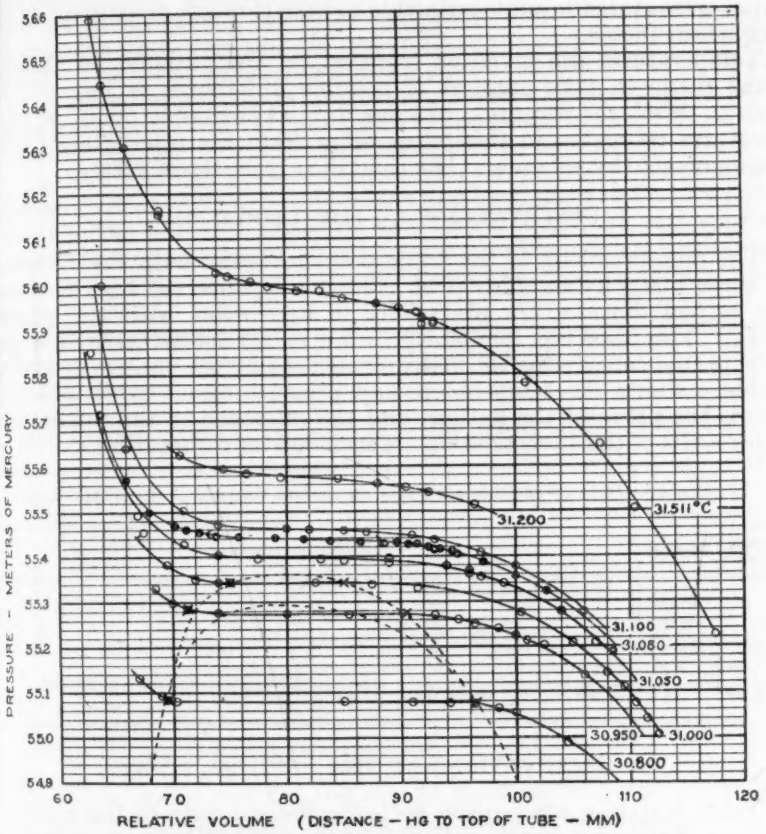


FIGURE 3.—*Isothermals for carbon dioxide in the critical region*

○ represents data on sample No. 1. ● represents data on sample No. 2. × point at which the carbon dioxide surface or band was either at the top or the bottom of the space. ( ) on the isotherm at 31.08° C. indicate that at volumes between these marks, fog was observed throughout the sample, while it could not be seen when the volume was outside these limits.

If this belief is correct the upper dotted curve in Figure 3 is not the true saturation curve, even though it was drawn approximately through the crosses which represent the average relative volume for the whole sample when the meniscus or band was either at the bottom or the top of the space occupied, but the lower dotted curve represents more nearly the state of the two phases under saturation conditions; that is, at the meniscus.

VII. MEASUREMENTS BY OTHER OBSERVERS

Measurements of vapor pressure by various observers are comparable only when both pressures and temperatures are expressed in units reducible to a common basis.

The pressure measurements quoted for comparison in the present paper were stated in units reducible to bars through multiplication by a constant factor.

Temperatures are given as reported by the authors, no attempt being made to take account of possible differences in temperature scales. With the exception of some data at the triple point, all temperatures tabulated in this paper differ from the international temperature scale by an amount less than the experimental error.

1. OBSERVATIONS AT THE TRIPLE POINT

The measurements of the triple point pressure, with the exception of those made by Faraday, who consistently observed high pressures for carbon dioxide, are practically in agreement with the present work. The observed temperatures are in agreement as well as can be expected considering the instruments used by the various observers. Table 4 shows the temperature and pressure observed at the triple point, the name of the author, and the reference to the publication. The results of this investigation are included for comparison.

TABLE 4.—*Data of various observers on carbon dioxide at the triple point*

Temperature	Pressure	Observer and reference
°C.	*Atmospheres*	
−57	5.31	Faraday, Trans. Roy. Soc., London, p. 155, 1845.
−56.7	5.1	Villard and Jarry, Compt. rend., vol. 120, p. 1413, 1895.
−56.24	5.10	Kuenen and Robson: Phil. Mag. (6) vol. 3, p. 149, 1902.
−56.4	5.11	Zeleny and Smith, Phys. Rev., vol. 24, p. 42, 1907; Phys. Zs., vol. 7, p. 667, 1906.
−56.60	5.112	Values from the present investigation.

2. OBSERVATIONS AT THE CRITICAL POINT

Table 5 gives a comparison with the present data of the results of various observers for carbon dioxide at the critical state.

Verschaffelt (1896) observed the capillary rise of the carbon dioxide in a glass tube a few tenths millimeter in diameter, at various temperatures up to 30° C. and extrapolated the data to a temperature at which the rise was zero. This he interpreted as the critical temperature.

Kuenen (1897) and Keesom (1903) observed the temperature at which the meniscus disappeared, and interpreted this as the critical temperature.

Von Wesendonck (1903) found that by repeated inversion of the vertical containing tube, a uniformly distributed fog was formed in the carbon dioxide in the temperature range 30.95° to 31.7° C. This fog remained indefinitely. Above 31.7° C. it decreased until at 32° C. it had entirely vanished.

Onnes and Fabius (1907) reported the critical temperature of carbon dioxide to be 30.985° C. The disappearance or the appear-

ance of the meniscus with slow heating or cooling occurred at temperatures which differed by only 0.02° C. The carbon dioxide used by them was first purified until the molecular proportion of impurities was estimated to be less than 3 parts in 10,000, after which it was fractionally distilled and sublimed.

Bradley, Browne, and Hale (1908) used the method of preparing carbon dioxide which was followed in preparing material for the present investigation, with the exception that they used sulphuric acid in the first drier and did not sublime the carbon dioxide. They obtained material which contained 1 part in 30,000 or 40,000 of gases not absorbed in potassium hydroxide solution. They give the critical temperature as 31.26° C., the mean of the two temperatures at which the meniscus disappeared or appeared differing by 0.08° C.

Cardoso and Bell observed the critical temperature and pressure of two samples of carbon dioxide which had been purified first by passing through five flasks of sulphuric acid and a long tube of phosphorus pentoxide, and second by 10 sublimations. The critical constants for one sample were found to be 31.00° C. and 72.77 atmospheres, for the other 31.00° C. and 72.90 atmospheres. They used a closed end nitrogen manometer and a calibrated mercury-in-glass thermometer. They estimated the accuracy of their results as 0.1° C. and 0.1 atmosphere.

TABLE 5.—*Data of various observers on carbon dioxide at the critical point*

t_c	p_c	Observer and reference
°C.	*atmospheres*	
30.92	73	Andrews, Trans. Roy. Soc. London, vol. 159, II, p. 575, 1869.
31	.....	Hautefeuille and Cailletet, Compt. rend., vol. 92, p. 840, 1881.
31.9	77	Dewar, Phil. Mag., vol. 18, p. 210, 1884.
31.35	72.9	Amagat, Compt. rend., vol. 114, p. 1093, 1322, 1892.
31.40	.....	Chappuis, Compt. rend., vol. 118, p. 976, 1894.
31.7	.....	Villard, J. phys. (3), p. 441, 1894.
31.0	.....	Verschaffelt, Versl. Kon. Akad. Amst. p. 94, 1896; Comm. Leiden, No. 28.
31.1	73.26	Kuenen, Phil. Mag. (5), vol. 44, p. 179, 1897.
31.4	.....	De Heen, Bull. Acad. Roy. Belgique, vol. 31, pp. 147, 879, 1896.
30.95 to 31.7	.....	Von Wesenbonck, Verh. deutsch Phys. Ges., vol. 5, p. 238, 1903.
30.98	72.93	Keesom, Versl. Kon. Akad. Amst., pp. 391, 533, 616, 1908; Comm. Leiden No. 88, 1903
31.12	.....	Brinkmann, Brinkmann Diss. Amst., 1904.
30.985	.....	Onnes and Fabius, Versl. Kon. Akad. Amst., p. 44, 1907; Proc. Kon. Akad. Amst., vol. 10, p. 215, 1907–8; Comm. Leiden No. 98, 1907.
31.26	.....	Bradley, Browne, and Hale, Phys. Rev., vol. 26, p. 470, 1908.
31.10	73.00	Dorsman, Dorsman Diss. Amst., 1908.
31.00	72.85	Cordoso and Bell, J. chim. phys., vol. 10, p. 500, 1912.
30.97	.....	Hein, Zs. physik. chem., vol. 86, p. 385, 1913–14.
30.96	.....	Kennedy and Meyers, Ref. Eng., vol. 15, p. 125, 1928.

Hein used the same method of preparing the carbon dioxide as Bradley, Browne, and Hale, but used apparatus entirely of glass, the only ground joint being in the stopcock in the dropping funnel. He estimated that the carbon dioxide contained not more than 1 part in 30,000 of air or other gas. The vapor of boiling propylchloride was used to maintain constant temperatures; and a calibrated thermometer divided in 0.1° C was used to measure temperatures.

The more accurate of the observations in Figure 5 indicate that the critical temperature is between 30.95° and 31.05° C. For prac-

tical purposes it probably will be sufficient to use 31.0° C. for which the corresponding calculated pressure (equation (6), Sec. VIII of this paper) is 72.80 atmospheres or 73.76 bars.

3. REVIEW OF VAPOR PRESSURE MEASUREMENTS

Onnes and Weber [15] measured the vapor pressure of the solid in the temperature range −183° to −135° C. A form of Knudsen's absolute manometer was used for the lower pressures.

A hot wire manometer which had a greater sensitivity than the Knudsen manometer was used for the higher pressures.

Their data on vapor pressure are precise to about 5 per cent or better at the lower temperatures and to a few tenths of a per cent at the higher temperatures.

The fact that their values at liquid air temperatures appear to be too high indicates that the samples contained traces of noncondensing impurities too small to be appreciable at the higher temperatures. This is confirmed by the fact that after the sample had warmed up and stood for a few days, the residual pressure at −200° C. increased from 0.007 to 0.016 microbars. A second series of measurements was corrected for this increase to make it comparable with the first.

Since boiling liquid baths of ethylene, methane, and oxygen were used, it is to be expected that the observed vapor pressure would be low because the thermometer can not be placed near the coldest part of the sample; that is, at the surface of the bath. In fact such is the case at the upper end of the temperature range where the measured pressure is relatively large (1,400 microbars), the observed values being about 1 per cent lower than the values calculated from equation (9), Section VIII of this paper, which are in agreement with calorimetric data and with vapor pressure measurements at higher temperatures. This discrepancy corresponds to about 0.07° C.

The thermal molecular pressure correction discussed in detail by Knudsen [16] becomes appreciable at temperatures below −140° C., and in the range −150° to −165° C. is uncertain.

Siemens [17] measured temperatures in the range −128° to −77° C. with a platinum resistance thermometer. The sample was in a container somewhat similar to the container (type 3) Figure 2 except that one side of the manometer was evacuated. The inside diameter of the manometer was 10 mm. The apparatus was evacuated through a side tube and carbon dioxide, generated from sodium bicarbonate and sulphuric acid, admitted to the apparatus. The carbon dioxide was purified by at least three sublimations. After each sublimation gaseous impurities were pumped out while the carbon dioxide was at liquid air temperature.

For the observations at temperatures within a few degrees of the normal sublimation point, the sample was placed in a bath which consisted of a thin mixture of carbon dioxide snow and alcohol rapidly stirred by a propeller. Air was admitted to the top of the bath so that the temperature was lowered below the sublimation point. Before a reading was to be taken the stirrer was stopped, thus allowing the solid

[15] Comm. Phys. Lab. Univ. Leiden Nos. 137b and 137c, 1913; Proc. K. Akad. Wetensch. Amst., vol. 16I, pp. 215 and 445, 1913.
[16] Ann. Physik (4), vol. 31, pp. 205 and 633, 1910, and (4), vol. 33, p. 1435, 1910.
[17] Ann. Physik (4), vol. 42, p. 871, 1913.

to settle with a consequent reduction in the evaporation and an increase in the temperature of the bath. Siemens believed that this expedient produced a bath warmer at the top. Although thermal conduction down the walls would tend to warm the bath from the top, yet the presence of air would accelerate the evaporation of carbon dioxide from solution, and it is a debatable question whether the surface of the bath was actually warmer than the remainder of the bath. Even if the attempt to make the top of the bath the warmest portion were successful, the temperature of the sample which is probably in poor thermal contact with the bath would lag considerably behind the rising bath temperature with consequent low observed pressures. The question of lag has been discussed in Section III of this paper.

For lower temperatures a large copper block was hung over liquid air in a Dewar flask. This block contained two wells filled with alcohol or pentane, in which the thermometer and the tube containing the sample of carbon dioxide were immersed. The sides and upper surface of this block were packed with insulating material. The temperature was controlled by raising or lowering the vessel containing the liquid air. Better observations are to be expected with this bath than with the former.

Henning [18] at the Physikalisch Technische Reichsanstalt measured the vapor pressure in the temperature range $-81°$ to $-78°$ C. For this purpose he used a bath [19] of petroleum ether in a silvered Dewar flask. The bath was cooled by a regulated stream of liquid air which was delivered to one side of a U tube, and, after evaporation, was expelled from the other side. This U tube, together with a screw propeller, was inclosed in a porcelain tube which had holes in its side at several different heights. The petroleum ether was drawn into the botton of the porcelain tube and forced past the U tube and out through the holes in the side of the porcelain tube. With only one exception the readings of the two platinum resistance thermometers used in the bath agreed within two or three hundredths degree.

The sample of carbon dioxide was contained in a glass apparatus only slightly different from that used by Siemens, the two arms of the manometer being separated and their open lower ends immersed in a dish of mercury. The manometer was read with a cathetometer readable to 0.01 mm. The sample of carbon dioxide was prepared by heating sodium bicarbonate and purified by numerous sublimations under reduced pressure.

Henning and Stock [20] measured the vapor pressure of carbon dioxide in the temperature range $-110°$ to $-80°$ C., with the aid of the same design of bath previously used by Henning. The thermometer of pure platinum used for these measurements had been carefully calibrated by comparison with a gas thermometer. The value given for the normal sublimation point is $-78.52°$ C. The samples of carbon dioxide were obtained both from commercial tanks and by the heating of sodium bicarbonate previously evacuated. The samples from each source were purified by alternately subliming in liquid air and pumping off noncondensing gases with a vacuum pump three times for the first source and one for the second.

[18] Ann. d. Phys. (4), vol. 43, p. 282, 1914.
[19] Zeits. fur Inst., vol. 33, p. 33, 1913.
[20] Zeits. fur Phys., vol. 4, p. 226, 1921.

The measurements at the Reichsanstalt were repeated by Heuse and Otto [21] in connection with a comparison between the international and the thermodynamic temperature scales. For the measurements at the normal sublimation point of carbon dioxide they used the same constant temperature bath previously used by Henning. The vapor pressure thermometer was improved over previous designs by the inclosure of the stem in a vaccuum jacket which extended from the portion at room temperature to near the end of the portion immersed in the bath. A bulb of about 1 cm^3 was left exposed to the bath. This insured that the bulb contained the coldest part of the sample, and consequently its temperature would correspond to the pressure measured. Two platinum resistance thermometers of the strain-free type were used as well as a helium gas thermometer which could at the normal sublimation point of carbon dixide be used either as a constant volume or constant pressure thermometer. The manometer was supplied with one fixed platinum point on the side connected to the gas thermometer and a series of fixed points on the other side so that the mercury could be adjusted on both sides of the manometer to optical contact with a pair of fixed points whose vertical distance had been measured. Their first series of measurements indicated the temperature of the normal sublimation point to be −78.483° and −78.523°, while the second series gave −78.471° and −78.509° C., respectively, on the thermodynamic and international scales.

Bridgeman [22] measured the vapor pressure of carbon dioxide at 0° C. Four piston gages were specially calibrated with an 8 m mercury column for this purpose. Groups of observations with these gages differed by only 1 part in 10,000. The process of purification is not described in detail, but the average difference observed for two samples is only 1 part in 40,000. The value given as a final mean (26,144.7 ± 1.0 mm) differs only about 1 part in 10,000 from the value (26,141.7 mm) calculated from equaton (6) and 2 parts in 10,000 from the mean of the observed values in this investigation.

Table 6 lists the vapor pressure observations which have been given weight in obtaining an equation for representing the vapor pressure as a function of temperature. The table gives also the corresponding values calculated from that equation, and the differences between the observed and calculated values.

---

[21] Ann. Physik (ser. 5) vol. 9, p. 486, 1931; vol. 14, pp. 181 and 185, 1932.
[22] J. Am. Chem. Soc. vol. 49₁, p. 1174, 1927.

TABLE 6.—*Vapor pressure measurements by other observers*

ONNES AND WEBER[9]

Observed temperature	Observed pressure	Calculated pressure	$100\times\frac{p_{obs.}-p_{calc.}}{p_{calc.}}$	$\theta_{obs.}-\theta_{calc.}$
° *C.*	*Microbars*	*Microbars*	*Per cent*	° *C.*
−183.0	0.008	0.005	58	−1.5
−179.60	.026	.019	36	−1.1
−175.37	.106	.087	22	−.6
−171.01	.404	.359	12	−.36
−168.83	.791	.699	13	−.37
−167.04	1.310	1.182	11	−.36

WEBER

−168.83	0.802	0.699	15	−0.47
−164.03	3.00	2.75	9.1	−.31
−163.19	3.76	3.45	9.0	−.32
−161.39	5.97	5.54	7.8	−.29
−159.72	8.80	8.49	3.7	−.15
−158.55	12.23	11.37	7.5	−.31
−155.00	27.96	26.58	5.2	−.22
[1] −151.46	47.88	58.90		
−152.46		47.27	1.3	−.06
−148.27	117.7	116.0	1.5	−.07
−145.44	205.0	205.4	−.2	.01
−143.07	323.8	325.0	−.4	.02
−140.63	509.6	512.0	−.5	.03
−138.69	720.0	726.0	−.8	.05
−136.78	1,001.8	1,013.7	−1.2	.07
−134.67	1,430.5	1,449.3	−1.3	.08
−129.29	5,257	3,431	54	−3.8
−129.28	5,263	3,436	54	−3.8

HENNING

	mm	*mm*		
−81.144	610.6	610.83	−0.04	0.005
−80.772	630.3	630.23	.01	−.001
−79.822	682.4	682.25	.02	−.002
−79.107	724.3	723.85	.06	−.007
−78.584	756.1	755.68	.06	−.007
−78.485	761.4	761.85	−.06	.007

BRIDGEMAN

0	26,144.7	26,141.7	0.01	−0.004

SIEMENS

−127.21	3.50	3.51	−0.3	0.02
−122.12	7.36	7.34	.3	−.02
−117.78	13.09	13.18	−.7	.05
−116.34	15.79	15.88	−.6	.04
−113.52	22.65	22.65	0	0
−110.57	32.19	32.37	−.6	.05
−106.64	50.39	50.96	−1.1	.10
−101.58	88.44	88.79	−.4	.04
−99.28	112.68	112.92	−.2	.02
−98.07	127.77	127.81	0	0
−95.03	172.9	173.12	−.1	.01
−92.66	217.1	217.72	−.3	.03
−89.89	283.1	282.40	.3	−.03
−87.59	348.9	348.39	.1	−.02
−87.10	364.1	364.08	0	0
−84.47	459.4	459.38	0	0
−82.61	538.4	539.39	−.2	.02
−81.87	573.2	574.47	−.2	.03
−80.86	622.7	625.60	−.5	.06
−80.05	667.1	669.43	−.3	.04
−79.60	692.1	694.94	−.4	.05
−79.06	723.0	726.67	−.5	.06
−78.47	759.7	762.77	−.4	.05
−77.39	830.1	832.99	−.3	.04

[1] This temperature appears to be in error by 1° C.

TABLE 6.—*Vapor pressure measurements by other observers*—Continued

HENNING AND STOCK

Observed temperature	Observed pressure	Calculated pressure	$100\times\frac{p_{obs.}-p_{calc.}}{p_{calc.}}$	$\theta_{obs.}-\theta_{calc.}$
° C.	*Microbars* *mm*	*Microbars* *mm*	*Per cent*	° C.
−109.74	35.7	35.70	0	0
−108.73	40.1	40.18	−0.2	0.018
−98.89	117.7	117.54	.1	−.013
−87.91	350.3	350.60	−.1	.010
−108.97	38.9	39.07	−.4	.036
−102.96	76.6	76.50	.1	−.012
−95.92	158.7	158.58	.1	−.009
−87.91	338.5	338.47	0	−.001
−80.05	669.9	669.43	.1	−.008

HEUSE AND OTTO

−78.523	760.0	759.45	0.07	−0.009
−78.509	760.0	760.33	−.04	.005

References to papers not already discussed which contain data on the vapor pressure of carbon dioxide are listed below.[23] A few of these contain data on the solid, but have been given no weight in the determination of the constants in the empirical equation.

Some of the more accurate measurements on the liquid are compared with the results given in this paper in Figure 4. The dotted curve indicates the percentage error corresponding to an error of 0.5° C. The zero line has been drawn sufficiently wide to include all the observations on samples in glass used in the present investigation.

The results of Jenkin and Pye shown in Figure 4 are unique in being the only measurement of the vapor pressure of carbon dioxide by the dynamic method.

[23] List of references on the vapor pressure of carbon dioxide.

Observer	Reference
Faraday	Trans. Roy. Soc., London, p. 155, 1845; Faraday's Researches in Chemistry and Physics (Univ. London Press, 1859).
Regnault	Relation des Experiences, vol. 2, p. 618, 1862 (Mem. Acad. Sci. Paris, vol. 26).
Andrews	Trans. Roy. Soc. London, vol. 159, II, p. 575, 1869; Scientific Papers of Thomas Andrews (MacMillan & Co. 1889).
Andrews	Phil. Mag. (5), vol. 1, p. 78, 1876; Ann. chim. phys. (5), vol. 8, p. 555, 1876.
Pictet	Arch. sci. phys. Nat. Geneve, vol. 61, p. 91, 1878; Ann. chim. phys. (5), vol. 13, p. 212, 1878.
Amagat	Ann. chim. phys. (6), vol. 29, p. 136, 1893; J. phys. (3), vol. 1, p. 288, 1892; Compt. rend., vol. 114, pp. 1093 and 1322, 1892.
Villard and Jarry	Compt. rend., vol. 120, p. 1413, 1895.
Villard	Ann. chim. phys. (7), vol. 10, p. 387, 1897.
Kuenen	Phil. Mag. (5), vol. 44, p. 179, 1897.
duBois and Wills	Verh. d. Ges., vol. 1, p. 168, 1899.
Holborn	Ann. Physik, vol. 6, p. 253, 1901.
Kuenen and Robson	Phil. Mag. (6), vol. 3, p. 149, 1902.
Lange	Z. ang. Chem., vol. 16, p. 514, 1903.
Keesom	Comm. Phys. Lab. Univ. Leiden No. 88, 1903; Proc. Kon. Akad. Amst., vol. 6, II, p. 565, 1904.
Zeleny and Smith	Phys. Zts., vol. 7, p. 667, 1906; Phys. Rev., vol. 24, p. 42, 1907.
Zeleny and Zeleny	Phys. Zts., vol. 7, p. 716, 1906; Phys. Rev., vol. 23, p. 308, 1906.
Nernst (published by Falck)	Phys. Zts., vol. 9, p. 435, 1908.
Jenkin and Pye	Trans. Roy. Soc. London, vol. 213, p. 67, 1913.
Keyes Townshend and Young	Jour. Math. and Phys., vol. 1, p. 243, 1922.

VIII. EMPIRICAL REPRESENTATION OF THE DATA

1. LIQUID CARBON DIOXIDE

For the representation of vapor pressure, an equation of the form

$$\log \frac{p}{p_0} = \frac{\theta-\theta_0}{\theta}\left\{A - B\,\frac{\theta-\theta_0}{\theta_0} + C\left(\frac{\theta-\theta_0}{\theta_0}\right)^2\right\} \qquad (1)$$

has been used by Cragoe,[24] where p and p_0 are, respectively, the observed pressure and the pressure at some standard temperature and θ and θ_0 are the corresponding absolute temperatures. In order to represent the measurements of the vapor pressure of liquid carbon dioxide within the limits of accuracy of the observations, it was necessary to add two terms involving higher powers of $\frac{\theta-\theta_0}{\theta_0}$.

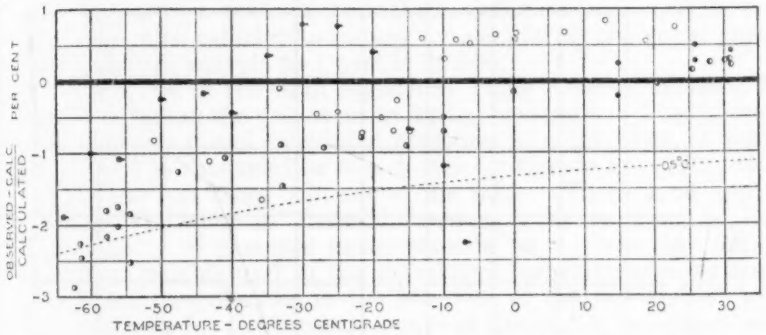


FIGURE 4.—*Comparison of the measurements on liquid by various observers*

The dotted curve shows the deviation in per cent of the pressure corresponding to an error of 0.5° C. The points shown are:
● Kuenen.
◑ Kuenen and Robson.
◐ Keesom.
▸ Zeleny and Smith.
○ Jenkin and Pye.

With the addition of these two terms, the choice of θ_0 as 0° C., and an algebraic transformation, the equation

$$\log p = 1.542235 + \frac{1}{273.10+t}(3.136105\,t + 0.000578554\,t^2 + 2.77120\,t^3\,10^{-5} + 3.19406\,t^4\,10^{-7} + 3.17316\,t^5\,10^{-9}) \qquad (2)$$

was obtained, t is the temperature in degrees centigrade on the international scale, and p is the pressure in bars.

Another equation has been obtained through graphical representation of the data. The values of $\theta \log p$ obtained from the observa-

[24] Int. Critical Tables, vol. 3, p. 228, McGraw Hill Book Co.

tions are approximately a linear function of temperature as may be deduced from the fact that the well-known equation

$$\log p = a - \frac{b}{\theta} \tag{3}$$

where a and b are constants, is a fair approximation. Consequently, $\theta\ (a - \log\ p)$ has an almost constant value. This quantity was plotted as ordinate with the square of the absolute temperature as abscissa. The points plotted lay on a curve which had a point of inflection and a form approximately that of a cubic. When a value of a was chosen such that the slope of the curve was zero at the point of inflection as in Figure 5, the curve was symmetrical about

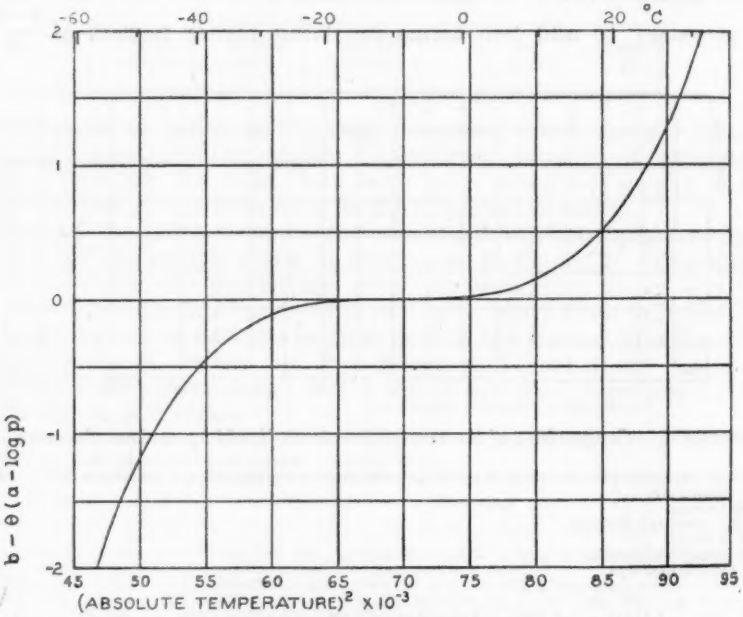


FIGURE 5.—*Term subtracted from b in equation (6).*

the point of inflection within the accuracy of the data. The position of the point of inflection was determined with sufficient accuracy by plotting on separate large semitransparent sheets of paper the points on the opposite sides of the point of inflection and superimposing the two parts of the curve thus formed.

It was found that the equation

$$\theta(a - \log\ p) = b - c(\theta^2 - \theta_1^2)^3 \tag{4}$$

where c is a constant and θ_1 is the temperature at the point of inflection, represented the data within about 1 part in 2,000, but that a consistent deviation from the observed values still existed, the curve

in Figure 5 being steeper at the extremities than would be indicated by equation (4). This led to the use of the equation

$$\theta(a-\log p)=b-my(10^{ny^2}-1) \tag{5}$$

or

$$\log_{10}p=a-\frac{1}{\theta}\{b-my(10^{ny^2}-1)\} \tag{6}$$

where for liquid carbon dioxide with p in bars

$a=4.674193$
$b=855.352$
$m=1.131\times10^{-4}$
$n=4.7\times10^{-10}$
$y=\theta^2-\theta_1^2$
$\theta_1^2=69{,}700$ $\quad(\theta_1=264.01)$

The term which has been added to equation (3) is relatively small (0.3 per cent of b or less for liquid carbon dixoide), and the use of a table of squares, a table of logarithms, and a slide rule yields values of this term with sufficient accuracy for calculating the vapor pressure of liquid carbon dioxide to 1 part in 10,000.

The pressures in the sixth column of Table 1 were calculated from equation (6) using the values given for the constants. The differences between observed and calculated pressures in millimeters, in parts in 100,000, and in thousandths of a degree centigrade are given, respectively, in the last three columns of the table. There is no apparent consistent variation in these differences with temperature. The reproducibility of pressure measurements on a given day indicates that an appreciable part of the differences for different days may be due to small irregularities in the behavior of the Wheatstone bridge used, especially for the measurements at the higher temperatures.

Differentiation of equation (6) gives

$$\frac{0.4343}{p}\frac{dp}{d\theta}=\frac{1}{\theta^2}[b-my(10^{ny^2}-1)]+2m[10^{ny^2}(4.605\ ny^2+1)-1] \tag{7}$$

The values of pressure and of $dp/d\theta$ for liquid carbon dioxide given in the appendix to this paper have been calculated from equations (6) and (7), using the constants already given.

Figure 6 gives an intercomparison between values calculated from equations (2) and (6), and groups of observed values. The upper part of the figure shows deviations from equation (2) and the lower part shows deviations from equation (6). The cross represents the mean of observations made on sample No. 1 at 0° C. at the Massachusetts Institute of Technology. The solid black circle at 0° C. represents the mean of the observations by Bridgeman.[25] The point is shown in this figure since the accuracy of his results and the agreement with this investigation are better than can be indicated on the more compressed scale used for other observations in Figure 4. The remaining circles represent observations made at this bureau. The point at −55° C. which is omitted in the upper part of the figure, represents only a single observation; its percentage deviation is rela-

[25] See footnote 22, p. 396.

tively large, but corresponds to an error of only 0.011° C. in the temperature. Each of the other circles represents the mean of several observations. The values for plotting these points were obtained by dividing the values in the eighth column of Table 1 into groups covering small temperature ranges and taking a mean of the values in each group, weighted as indicated in the fifth column of the table. The figure shows that both equations represent the data almost equally well, although near the critical temperature equation (6) appears to be slightly better. This equation probably represents the vapor pressure of the samples observed within 1 or 2 parts in 10,000. The values of $dp/d\theta$ calculated from the two equations differ by less than 1 part in 1,500 in the temperature range −56° to 25° C.; but

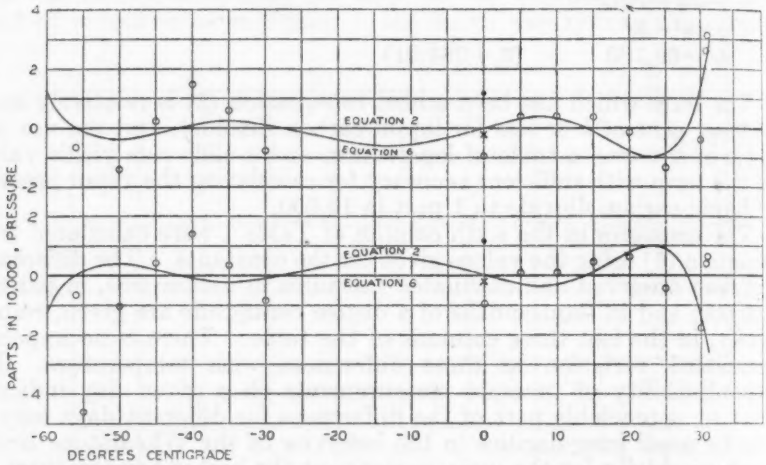


FIGURE 6.—*Intercomparison of equations (2) and (6) and observed values*

× represents mean of observations at 0° C. on sample No. 1 by Massachusetts Institute of Technology. ○ mean of observations at this bureau. Point at −55° C., is a single observation and is omitted in the upper part of the figure. ● mean of measurements by O. C. Bridgeman

at 31° C., equation (6) yields the larger value by 0.5 per cent. No exact estimate can be made of the accuracy of the values of $dp/d\theta$ calculated from equation (6), but it seems fairly certain that the accuracy is better than 1 part in 1,000 except near the critical temperature and that the error does not exceed 0.5 per cent at that point. This accuracy is considered ample for use in the Clapeyron-Clausius relation

$$L/\theta=(V-v)dp/d\theta \tag{8}$$

since the latent heat and difference between the specific volumes of the vapor and liquid approach zero as a limit at the critical temperature.

2. SOLID CARBON DIOXIDE

Over the temperature range within which accurate vapor pressure data have been obtained for solid carbon dioxide the results can be represented in bars by the equation

$$\log p=6.92804-\frac{1}{\theta}[1{,}347.00-1.167\ (\theta^2-35{,}450)^3 10^{-12}] \tag{9}$$

The calculated pressures in the fifth column of Table 2 as well as the values of pressure and of $dp/d\theta$ for solid carbon dioxide given in the appendix to this paper have been calculated from equation (9). The differences between the pressures observed in this investigation and the calculated pressures are given in the last three columns of Table 2.

These differences are represented graphically in Figure 7 with the exception of two values observed March 20, 1931, which are discarded

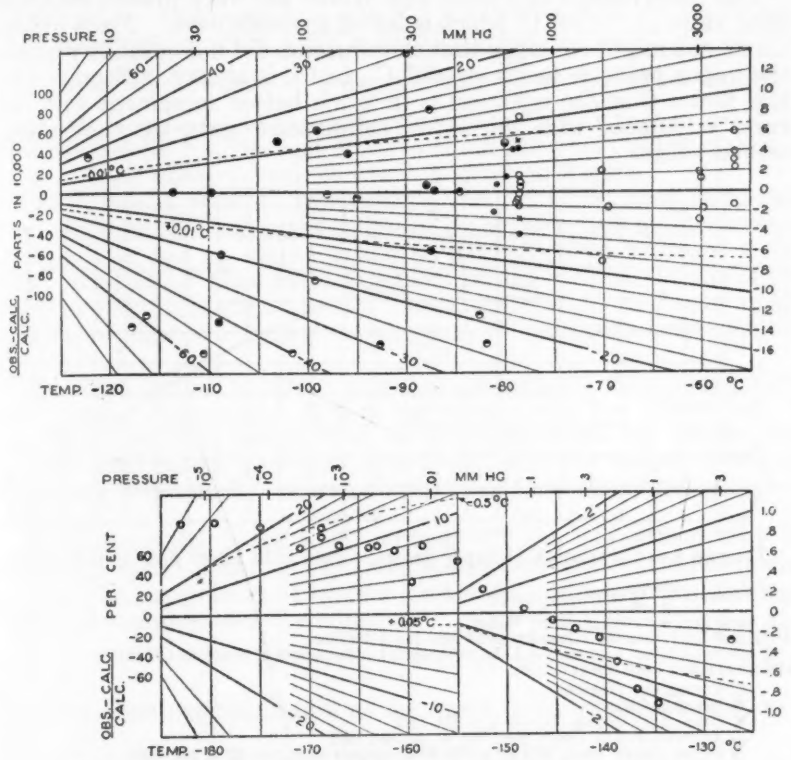


FIGURE 7.—*Comparison of observed pressures with equation (9)*

The dotted curves show the deviation in pressure corresponding to the indicated error in temperature. The points shown are:

- ○ this investigation (upper chart).
- • Henning, Ann. Physik (ser. 4), vol. 43, p. 282, 1914.
- ● Henning and Stock, Zs. Phys., vol. 4, p. 226, 1921.
- ◓ Siemens, Ann. Physik (ser. 4), vol. 42, p. 871, 1913.
- ○ Weber, Leiden Comm. No. 137c, 1913 (lower chart).
- ○ Onnes and Weber, Leiden Comm. No. 137b, 1913 (lower chart).
- × Heuse and Otto, Ann. Physik (ser. 5), vol. 9, p. 486, 1931, and vol. 14, pp. 181 and 185, 1932.

(see footnote to Table 2). The coordinates have been chosen to give as nearly as possible a uniform dispersion of the points throughout the temperature range. The dotted lines indicate the errors in temperature corresponding to percentage errors in the pressure while the scale of pressures at the top makes possible an estimate of the absolute value of the pressure differences. These points form four groups covering small temperature intervals in the temperature range $-56.6°$ to $-80°$ C. If the mean of the points in each group, weighted as

indicated in Table 2, is taken, the maximum deviation from the equation for these means is 2 parts in 10,000.

It will be seen that these observed values and equation (9) are both in excellent agreement with the work at the Reichsanstalt. There is also good agreement at the lower temperatures with the observations of Siemens, but his observations near the normal sublimation point are so low as to be off the scale used in the figure. This discrepancy is discussed in part 3 of Section VII of this paper.

The observations of Onnes and Weber are very precise except for their value at −129° C. which is far off the scale used. From Figure 7 alone, one might conclude that the equation did not actually represent the vapor pressure below −100° C., but it is shown in Section IX of this paper that the equation is in much better agreement with pressures calculated with the aid of calorimetric data than are the observed values.

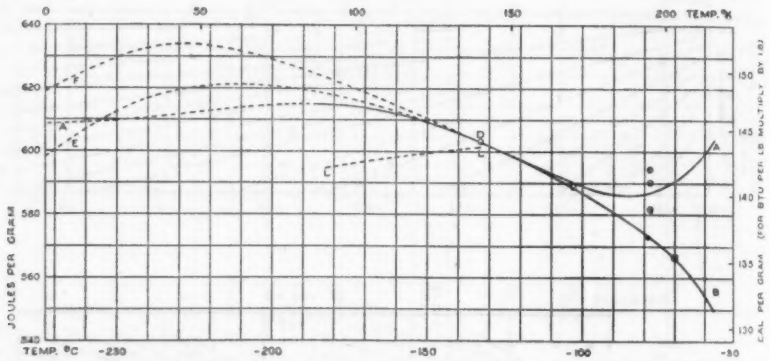


FIGURE 8.—*Correlation of vapor pressure data with latent heat of sublimation*

AA, values of $\frac{R\theta^2}{p}\frac{dp}{d\theta}$ from equation (9).

LL, same from equation given by Weber.

BDE and *BDF*, possible values for latent heat of sublimation.

□ calculated latent heat from *AA* and volumetric measurements of Maass and Mennie.

Observed latent heats are as follows:

○ Eucken and Donath.
● Maass and Barnes.
◐ Behn, Ann. Physik (4), vol. 1, p. 270, 1900.
◒ Andrews, J. Am. Chem. Soc., vol. 47, p. 1597, 1925.
◑ Favre, Compt. rend., vol. 39, p. 729, 1854; Liebig's Ann., vol. 92, p. 194, 1854.

(Other references given in the text.)

IX. CORRELATION OF THE VAPOR PRESSURE DATA WITH CALORIMETRIC DATA

It is desirable to correlate calorimetric data with the vapor pressure and to use this correlation as an aid in estimating the accuracy of the calculated values of the vapor pressure particularly at the lower temperatures where the percentage accuracy of the vapor pressure measurements is relatively poor.

From the exact Clapeyron-Clausius relation (see equation (8)) and the approximation, $V-v=\frac{R\theta}{p}$, which is sufficiently accurate at the lower temperatures, one obtains

$$L=\frac{R\theta^2}{p}dp/d\theta \qquad (10)$$

Values of $\frac{R\theta^2}{p} dp/d\theta$ for the solid were calculated from equation (9), plotted in Figure 8 as ordinates with temperature as abscissa, and represented by the curve AA.

Of the various observed values of latent heat represented in the figure, the two by Eucken and Donath [26] are probably the most accurate. The agreement between the various data presented in the figure confirms the claim of those authors for an accuracy of 0.1 or 0.2 per cent. The point at $-133.1°$ C. coincides with the curve AA, while the point at $-103.1°$ C. is slightly below the curve AA in consequence of the fact that $V-v$ departs from $\frac{R\theta}{p}$ at the higher temperatures. It is to be noted that the value for the latent heat at $-133.1°$ C. published by Eucken and Donath is 0.2 per cent smaller than the mean of their observed values which is given in Figure 8.

The square at $-70°$ C. represents a value of latent heat calculated from equation (8) using the value of $dp/d\theta$ obtained in the present investigation and an extrapolation to the saturation pressure of the value obtained by Maass and Mennie [27] for the specific volume of the vapor at about one atmosphere. This extrapolation was based on the assumption that at constant temperature PV varies linearly with the density.

The curve from B to D was drawn approximately through the three points under discussion. It is in agreement with the observation of the latent heat at the normal sublimation point by Maass and Barnes,[28] and except near the triple point, with the values chosen by Plank and Kuprianoff [29] in their correlation of the properties of carbon dioxide.

At temperatures lower than $-133.1°$ C., the latent heat may be calculated from Eucken and Donath's observed value at that temperature and an integration of specific heat data. For carbon dioxide at these low temperatures the equation

$$C_{p_{\text{gas}}} - C_{p_{\text{solid}}} = dL/d\theta \tag{11}$$

is a very close approximation to the exact thermodynamic relation

$$C_{p_{\text{gas}}} - C_{p_{\text{solid}}} = dL/d\theta - L/\theta + \theta\left[\left(\frac{\delta v}{\delta\theta}\right)_{p_{\text{gas}}} - \left(\frac{\delta v}{\delta\theta}\right)_{p_{\text{solid}}}\right] dp/d\theta. \tag{12}$$

For the purpose of this integration Eucken's [30] determinations of the specific heat at constant pressure for the solid were used. In the temperature range above $-170°$ C. these observations can be represented by the equation

$$\begin{aligned} C_{p_{\text{solid}}} &= 0.60 + 0.0033\theta, \text{j/g°C.} \\ &= 0.143 + 0.00079\theta, \text{cal/g°C., or Btu/lb°F.} \end{aligned} \tag{13}$$

Below this temperature integration was performed by choosing from a graph, the average differences between the specific heat for the gas and for the solid over a limited temperature range and multiplying

[26] Z. phys. Chem., vol. 124, p. 181, 1926.
[27] Proc. Roy. Soc., London, Ser. A, vol. 110, p. 198, 1926.
[28] Proc. Roy. Soc., London, Ser. A, vol. 111, p. 224, 1926.
[29] Beiheft Z. ges. Kälte-Ind. Reihe 1, Heft 1, 1929.
[30] Verhand. Deutschen phys. Gesell., vol. 18, p. 4, 1916.

by the temperature increment. Although the values of specific heat published by Maass and Barnes [31] differ somewhat from those by Eucken, it appears that a correction should be applied to their data especially at the higher temperatures for evaporation of part of the sample when warmed, since the solid did not fill the container entirely. Although the information available was insufficient for determining this correction accurately, it appears that the correction is of the proper magnitude to bring the two sets of data into substantial agreement.

The specific heat of the vapor is not well established at low temperatures by experimental values, the observed value at the lowest temperature being 0.768 joules per gram per °C., at 1 atmosphere and −75° C. by Heuse.[32]

Theoretical considerations have led various authors to believe that C_p for carbon dioxide vapor approaches $3.5R$ or 0.662 joules per gram per °C. as a limit at absolute zero. A graph of the available data plotted with specific heat and temperature as coordinates indicates that if this is the limit approached, $C_{p_{gas}}$ below −130° C. may for our purpose be considered equal to the limiting value. With this assumption

$$\int (C_{p_{gas}} - C_{p_{solid}}) d\theta$$

is represented by the curve DE in Figure 8.

The graph of experimental data mentioned does not determine the limiting value for $C_{p_{gas}}$. If, as is believed for hydrogen, the limit is $2.5R$, a smooth curve through the experimental data near saturation and through $2.5R$ at absolute zero is, to a first approximation, represented by assuming $C_{p_{gas}}$ equal to $0.473 + 7.5 \times ,10^{-6},\theta^2$. This assumption leads to the curve DF in Figure 8.

An integration of the function represented by the curve DF gives values for vapor pressure about 15, 3, and 0.3 per cent smaller at −190°, −170°, and −150° C., respectively, than those obtained from equation (9). The corresponding differences between values obtained from integration of the function represented by DE and those from equation (9) are about one-third as great. The curve BDE probably gives as good an estimate of the latent heat of sublimation as can be made from the available data.

Weber and Onnes [33] have shown that their measurements in the range −180° to −130° C. are very well represented by the equation

$$\log p = \frac{6007.9}{4.571}\frac{1}{\theta} + 1.75 \log \theta - \frac{0.009008}{4.571}\theta + 3.1700 \qquad (15)$$

Values of $\frac{R\theta^2}{p} dp/d\theta$ calculated from this equation are represented by the dotted curve LL. It is apparent that their observations are not in agreement with calorimetric data.

From this correlation of the data it appears that the vapor pressures calculated from equation (9), although considerably smaller at very low temperatures than the observed pressures, are not too small but may be slightly too large.

---

[31] See footnote 28, p. 405.
[32] Ann. Physik (4), vol. 59, p. 86, 1919.
[33] See footnote 15, p. 394.

It is to be noted that under conditions such as occur in the present case where the percentage accuracy of the observed vapor pressures decreases with decreasing temperature, the vapor pressure equation gives the quantity $\frac{1}{p}dp/d\theta$ with greater percentage accuracy than it does the quantity $dp/d\theta$ or even the vapor pressure itself. For example, two equations which gave at $-130°$ C. the same vapor pressures and the same values for $\frac{R\theta^2}{p}dp_2/d\theta$, yielded at $-190°$ C. vapor pressures differing by 15 per cent and values of $\frac{R\theta^2}{p}dp/d\theta$ differing by only 3 per cent.

X. CONCLUSIONS

The vapor pressure of liquid and solid carbon dioxide has been measured at this bureau in the range 31° to −79° C. The average deviation of the weighted observations from values calculated from an equation is 1.0 part in 10,000 for the liquid and 2.4 parts in 10,000 for the solid. These average deviations correspond to about 0.004° C. for both liquid and solid. The value of the vapor pressure at 0° C. calculated from the equation for the liquid is only 1 part in 10,000 less than that observed by O. C. Bridgeman.

The measurements near the normal sublimation point (−78.514° C.) are in agreement with those at the Reichsanstalt. The equation for the solid has been designed to represent also the measurements at temperatures below −79° C. by Henning and Stock, Siemens, and Onnes and Weber.

The values of vapor pressure given in the Appendix to this paper are considered accurate within 1 or 2 parts in 10,000 in the range 31° to −80° C., 1 part in 1,000 in the range −80° to −100° C., 1 per cent in the range −100° to −140° C., and about 20 per cent in the range −140° to −190° C.

The triple point pressure and temperature are $3{,}885.2 \pm 0.4$ mm and $-56{,}602 \pm 0.005°$ C., respectively.

The critical point temperature is considered to be between 30.95° and 31.05° C. For practical purposes the temperature may be assumed to be 31.00° C. for which the corresponding pressure is 73.76 bars (72.80 atmospheres or 55,330 mm).

Observations of pressure and relative volumes along several isotherms in the neighborhood of the critical point are given.

The values of $dp/d\theta$ in the Appendix obtained through differentiation of the vapor pressure equations for the liquid and the solids are considered accurate within 1 part in 1,000 in the range 25° to −100° C., and within about 0.5 per cent near the critical point. The differentiation of the vapor pressure equation for the solid leads to results which together with volumetric data from other laboratories make possible, through the Clapeyron-Clausius relation, a better estimate of latent heat of sublimation than has hitherto been made from such data. Such estimate is in agreement with the latent heat observed by Eucken and Donath. A graph (fig. 8) showing the relation between the latent heat and temperature is given. Values from the curve *BDE* of this graph are considered to represent the latent heat of sublimation within 1 per cent down to liquid air temperatures and within 2 or 3 parts in 1,000 in the range −80° to −150° C.

XI. ACKNOWLEDGMENTS

Acknowledgement is made to C. S. Taylor, who prepared and purified the carbon dioxide; to D. O. Burger for assistance in taking the observations in 1931.

XII. APPENDIX

The values in the following tables have been calculated from equations (6) and (9) given in the text or from their differential equations. The temperatures recorded have been corrected to the international temperature scale. The term "bar" is used in accordance with the usage now internationally accepted; that is, to indicate a pressure of 1,000,000 dynes per square centimeter or 0.96784 normal atmospheres. The term microbar is used to indicate a pressure of one dyne per square centimeter.

The error caused by linear interpolation between the pressure given every degree may be appreciable especially for the solid, but linear interpolation between the logarithms of these pressures will rarely introduce an error greater than a unit in the last decimal place given in the tables.

TABLE 7.—*Vapor pressure of solid carbon dioxide*

[In lbs. per in.^{2}, reduced to g=32.1740 ft. per sec.^{2}]

°F.	0	1	2	3	4	5	6	7	8	9
−210	0.022	0.020	0.018	0.016	0.015	0.014	0.012	0.011	0.010	0.009
−200	.053	.049	.045	.041	.038	.034	.031	.029	.026	.024
−190	.120	.111	.103	.095	.087	.080	.074	.068	.063	.058
−180	.255	.237	.220	.204	.190	.176	.163	.151	.140	.129
−170	.513	.480	.448	.419	.391	.364	.339	.316	.295	.274
−160	.984	.924	.867	.813	.763	.715	.670	.627	.587	.549
−150	1.804	1.701	1.603	1.511	1.423	1.339	1.260	1.186	1.115	1.048
−140	3.18	3.01	2.85	2.69	2.54	2.40	2.27	2.15	2.03	1.91
−130	5.40	5.13	4.87	4.62	4.39	4.16	3.95	3.74	3.54	3.36
−120	8.90	8.48	8.07	7.69	7.32	6.96	6.62	6.30	5.98	5.69
−110	14.25	13.61	13.00	12.40	11.84	11.30	10.78	10.28	9.80	9.34
−100	22.24	21.30	20.39	19.51	18.67	17.86	17.08	16.33	15.61	14.92
− 90	33.95	32.57	31.25	29.97	28.74	27.55	26.41	25.31	24.24	23.22
− 80	50.81	48.84	46.94	45.11	43.34	41.63	39.98	38.39	36.85	35.37
− 70	74.79	72.01	69.31	66.71	64.19	61.76	59.42	57.15	54.97	52.85

Triple point, −69.88° F.; 75.13 lbs./in.^{2}

TABLE 8.—*Vapor pressure of liquid carbon dioxide*

[In lbs. per in.^{2}, reduced to g=32.1740 ft. per sec.^{2}]

°F.	0	1	2	3	4	5	6	7	8	9
−60	94.75	92.61	90.51	88.44	86.40	84.40	82.43	80.50	78.61	76.74
−50	118.28	115.75	113.26	110.81	108.40	106.03	103.70	101.41	99.15	96.94
−40	145.90	142.94	140.02	137.15	134.33	131.55	128.81	126.12	123.46	120.85
−30	178.02	174.59	171.21	167.88	164.60	161.37	158.18	155.04	151.95	148.90
−20	215.09	211.15	207.26	203.42	199.64	195.91	192.23	188.60	185.03	181.50
−10	257.6	253.1	248.6	244.2	239.9	235.6	231.4	227.2	223.1	219.1
− 0	305.9	300.8	295.7	290.7	285.8	281.0	276.2	271.4	266.7	262.1
0	305.9	311.0	316.3	321.6	326.9	332.4	337.9	343.4	349.1	354.8
10	360.5	366.3	372.2	378.2	384.3	390.4	396.6	402.8	409.1	415.5
20	422.0	428.5	435.1	441.8	448.6	455.4	462.4	469.3	476.4	483.6
30	490.8	498.1	505.5	513.0	520.5	528.1	535.8	543.6	551.5	559.5
40	567.5	575.7	583.9	592.2	600.6	609.1	617.7	626.3	635.1	643.9
50	652.9	661.9	671.0	680.2	689.6	699.0	708.5	718.1	727.8	737.6
60	747.5	757.6	767.7	777.9	788.2	798.7	809.2	819.9	830.7	841.5
70	852.6	863.7	874.9	886.3	897.8	909.4	921.1	933.0	945.0	957.1
80	969.4	981.8	994.3	1,007.0	1,019.8	1,032.7	1,045.9	1,059.1	----------	----------

Critical point, 87.8° F.; 1,069.9 lbs./in.^{2}
Triple point, −69.88° F.; 75.13 lbs./in.^{2}

TABLE 9.—*Vapor pressure of solid carbon dioxide*

[Mercury column, density=13.5951 g/cm³]

[g=980.665]

PRESSURE IN MICRONS OF MERCURY

°C.	0	1	2	3	4	5	6	7	8	9
−180	0.013	0.008	0.006	0.004	0.003	0.0017	0.0011	0.0007	0.0005	0.0003
−170	.37	.27	.20	.14	.10	.074	.052	.037	.026	.018
−160	5.9	4.6	3.6	2.7	2.1	1.58	1.19	.90	.67	.50
−150	60.5	48.8	39.2	31.4	25.1	19.9	15.8	12.4	9.8	7.6
−140	431	359	298	247	204	168	138	113	92	75

PRESSURE IN mm OF MERCURY

−130	2.31	1.97	1.68	1.43	1.22	1.03	0.87	0.73	0.61	0.51
−120	9.81	8.37	7.46	6.49	5.63	4.88	4.22	3.64	3.13	2.69
−110	34.63	30.76	27.27	24.14	21.34	18.83	16.58	14.58	12.80	11.22
−100	104.81	94.40	84.91	76.27	68.43	61.30	54.84	48.99	43.71	38.94
−90	279.5	254.7	231.8	210.8	191.4	173.6	157.3	142.4	128.7	116.2
−80	672.2	618.3	568.2	521.7	478.5	438.6	401.6	367.4	335.7	306.5
−70	1,486.1	1,377.3	1,275.6	1,180.5	1,091.7	1,008.9	931.7	859.7	792.7	730.3
−60	3,073.1	2,865.1	2,669.7	2,486.3	2,314.2	2,152.8	2,001.5	1,859.7	1,726.9	1,602.5
−50								3,780.9	3,530.2	3,294.6

Triple point, −56.602±0.005° C.; 3885.2±0.4 mm.

TABLE 10.—*Vapor pressure of liquid carbon dioxide*

[Millimeters of mercury, density=13.5951 g/cm³]

[g=980.665]

°C.	0	1	2	3	4	5	6	7	8	9
−50	5,127.8	4,922.7	4,723.9	4,531.1	4,344.3	4,163.2	3,987.9	[1]3,818.2	[1]3,653.9	[1]3,495.0
−40	7,545	7,271	7,005	6,746	6,494	6,250	6,012	5,781	5,557	5,339
−30	10,718	10,363	10,017	9,679	9,350	9,029	8,716	8,412	8,115	7,826
−20	14,781	14,331	13,891	13,461	13,040	12,630	12,229	11,838	11,455	11,082
−10	19,872	19,312	18,764	18,228	17,703	17,189	16,686	16,194	15,712	15,241
−0	26,142	25,457	24,786	24,127	23,482	22,849	22,229	21,622	21,026	20,443
0	26,142	26,840	27,552	28,277	29,017	29,771	30,539	31,323	32,121	32,934
10	33,763	34,607	35,467	36,343	37,236	38,146	39,073	40,017	40,980	41,960
20	42,959	43,977	45,014	46,072	47,150	48,250	49,370	50,514	51,680	52,871
30	54,086	55,327								

[1] Undercooled liquid.

Critical temperature=31.0° C.

Triple point, −56.602±0.005° C.; 3885.2±0.4 mm.

TABLE 11.—*Vapor pressure of solid carbon dioxide*

[In absolute units]

PRESSURE IN MICROBARS

°C.	0	1	2	3	4	5	6	7	8	9
−180	0.017	0.011	0.008	0.005	0.003	0.002	0.0015	0.0010	0.0006	0.0004
−170	.49	.36	.26	.19	.14	.10	.07	.05	.03	.02
−160	7.9	6.1	4.7	3.6	2.8	2.10	1.59	1.19	.89	.66
−150	81	65	52	42	33	26.6	21.0	16.6	13.0	10.2
−140	574	478	398	329	272	224	184	150	123	100

PRESSURE IN BARS

−130	0.00308	0.00263	0.00225	0.00191	0.00162	0.00137	0.00116	0.00098	0.00082	0.00069
−120	.01311	.01145	.00997	.00868	.00753	.00652	.00564	.00486	.00419	.00359
−110	.04620	.04104	.03639	.03222	.02849	.02514	.02215	.01948	.01710	.01499
−100	.1397	.1258	.1132	.1017	.0912	.0817	.0731	.0653	.0583	.0519
−90	.3727	.3396	.3091	.2810	.2552	.2315	.2098	.1898	.1716	.1549
−80	.8962	.8243	.7575	.6955	.6380	.5847	.5354	.4898	.4476	.4086
−70	1.9813	1.8362	1.7006	1.5739	1.4555	1.3451	1.2422	1.1462	1.0568	.9736
−60	4.0971	3.8198	3.5593	3.3148	3.0854	2.8701	2.6684	2.4794	2.3023	2.1365
−50								5.0408	4.7066	4.3924

Triple point, −56.602±0.005° C.; 5.1798±0.0005 bars.

TABLE 12.—*Vapor pressure of liquid carbon dioxide*

[In bars]

°C.	0	1	2	3	4	5	6	7	8	9
−50	6.836	6.563	6.298	6.041	5.792	5.551	5.317	[1] 5.091	[1] 4.872	[1] 4.660
−40	10.059	9.694	9.339	8.994	8.659	8.332	8.015	7.707	7.408	7.118
−30	14.290	13.817	13.355	12.905	12.466	12.038	11.621	11.215	10.819	10.434
−20	19.706	19.106	18.519	17.946	17.386	16.839	16.304	15.782	15.273	14.775
−10	26.494	25.748	25.017	24.302	23.602	22.916	22.246	21.590	20.948	20.320
−0	34.853	33.940	33.045	32.167	31.306	30.463	29.637	28.827	28.033	27.255
0	34.853	35.783	36.732	37.700	38.686	39.691	40.716	41.760	42.824	43.908
10	45.013	46.139	47.286	48.454	49.645	50.857	52.093	53.352	54.635	55.942
20	57.27	58.63	60.01	61.42	62.86	64.33	65.82	67.35	68.90	70.49
30	72.11	73.76								

[1] Undercooled liquid.

Critical temperature=31.0° C.
Triple point, −56.602±0.005° C.; 5.1798±0.0005 bars.

TABLE 13.—*Vapor pressure of solid carbon dioxide*

[In kg/cm², g=980.665]

°C.	0	1	2	3	4	5	6	7	8	9
−140	0.00059	0.00049	0.00040	0.00034	0.00028	0.00023	0.00019	0.00015	0.00012	0.00010
−130	.00313	.00268	.00229	.00195	.00165	.00140	.00118	.00100	.00084	.00070
−120	.01334	.01165	.01015	.00883	.00766	.00664	.00574	.00495	.00426	.00366
−110	.04708	.04181	.03707	.03282	.02901	.02560	.02255	.01983	.01741	.01525
−100	.14249	.12833	.11543	.10370	.09302	.08334	.07456	.06661	.05942	.05293
−90	.3800	.3463	.3152	.2865	.2602	.2360	.2139	.1936	.1750	.1580
−80	.9139	.8405	.7724	.7092	.6506	.5963	.5460	.4994	.4564	.4167
−70	2.0204	1.8724	1.7341	1.6049	1.4843	1.3716	1.2667	1.1688	1.0776	.9928
−60	4.1779	3.8951	3.6295	3.3802	3.1462	2.9267	2.7210	2.5283	2.3477	2.1786
−50								5.1402	4.7994	4.4790

Triple point, −56.602±0.005° C.; 5.2818 kg/cm².

TABLE 14.—*Vapor pressure of liquid carbon dioxide*

[In kg/cm², g=980.665]

°C.	0	1	2	3	4	5	6	7	8	9
−50	6.9713	6.6925	6.4222	6.1601	5.9061	5.6600	5.4216	[1] 5.1909	[1] 4.9675	[1] 4.7515
−40	10.257	9.885	9.524	9.172	8.829	8.497	8.174	7.860	7.555	7.259
−30	14.572	14.089	13.618	13.159	12.711	12.275	11.850	11.436	11.032	10.640
−20	20.095	19.483	18.885	18.300	17.729	17.171	16.625	16.093	15.574	15.067
−10	27.016	26.255	25.510	24.781	24.069	23.368	22.684	22.015	21.361	20.721
−0	35.540	34.609	33.696	32.801	31.924	31.064	30.221	29.395	28.585	27.793
0	35.540	36.489	37.457	38.443	39.449	40.474	41.519	42.583	43.668	44.774
10	45.900	47.048	48.218	49.409	50.623	51.860	53.120	54.404	55.712	57.045
20	58.403	59.787	61.198	62.635	64.101	65.595	67.120	68.674	70.260	71.878
30	73.531	75.217								

[1] Undercooled liquid.

Critical temperature=31° C. Triple point, −56.602±0.005° C.; 5.2819 kg/cm².

TABLE 15.—*Vapor pressure of solid carbon dioxide*

[Density of mercury=13.5951, g=980.665]

[Temperatures in °C. below zero for even millimeters of mercury]

mm	0	1	2	3	4	5	6	7	8	9
400	86.045	86.016	85.988	85.960	85.932	85.904	85.876	85.848	85.821	85.794
410	85.766	85.738	85.710	85.683	85.656	85.628	85.601	85.574	85.547	85.520
420	85.493	85.466	85.439	85.412	85.385	85.358	85.331	85.304	85.278	85.251
430	85.225	85.198	85.172	85.146	85.120	85.094	85.067	85.041	85.015	84.989
440	84.963	84.937	84.911	84.885	84.860	84.834	84.809	84.783	84.757	84.731
450	84.706	84.681	84.656	84.630	84.605	84.580	84.555	84.530	84.505	84.480
460	84.455	84.430	84.405	84.380	84.355	84.330	84.306	84.281	84.257	84.232
470	84.207	84.183	84.159	84.134	84.110	84.086	84.062	84.037	84.013	83.989
480	83.965	83.941	83.917	83.893	83.869	83.846	83.822	83.798	83.774	83.750
490	83.727	83.703	83.680	83.656	83.633	83.609	83.586	83.562	83.539	83.516
500	83.493	83.470	83.447	83.424	83.401	83.378	83.355	83.332	83.309	83.286
510	83.263	83.240	83.218	83.195	83.172	83.149	83.127	83.104	83.082	83.059
520	83.037	83.015	82.993	82.970	82.948	82.926	82.904	82.881	82.859	82.837
530	82.815	82.793	82.771	82.749	82.727	82.706	82.684	82.662	82.640	82.618
540	82.597	82.575	82.554	82.532	82.510	82.489	82.467	82.446	82.425	82.403
550	82.382	82.360	82.339	82.318	82.297	82.275	82.254	82.233	82.212	82.191
560	82.170	82.149	82.128	82.107	82.087	82.066	82.045	82.024	82.004	81.983
570	81.962	81.941	81.921	81.900	81.880	81.859	81.839	81.818	81.798	81.777
580	81.757	81.737	81.716	81.696	81.676	81.655	81.635	81.615	81.595	81.575
590	81.555	81.535	81.515	81.495	81.475	81.455	81.435	81.416	81.396	81.376
600	81.356	81.337	81.317	81.297	81.277	81.258	81.238	81.219	81.199	81.180
610	81.160	81.140	81.121	81.102	81.083	81.064	81.044	81.025	81.005	80.986
620	80.967	80.948	80.928	80.909	80.890	80.871	80.852	80.833	80.814	80.795
630	80.776	80.757	80.739	80.720	80.701	80.682	80.663	80.645	80.626	80.607
640	80.588	80.570	80.551	80.533	80.514	80.496	80.477	80.459	80.440	80.422
650	80.403	80.385	80.367	80.348	80.330	80.311	80.293	80.275	80.257	80.239
660	80.220	80.202	80.184	80.166	80.148	80.130	80.112	80.094	80.076	80.058
670	80.040	80.022	80.004	79.986	79.968	79.950	79.933	79.915	79.897	79.879
680	79.862	79.844	79.826	79.809	79.791	79.774	79.756	79.738	79.721	79.703
690	79.686	79.668	79.651	79.634	79.616	79.599	79.581	79.564	79.547	79.530
700	79.512	79.495	79.478	79.461	79.444	79.426	79.409	79.392	79.375	79.358
710	79.341	79.324	79.307	79.290	79.273	79.256	79.239	79.222	79.205	79.189
720	79.172	79.155	79.138	79.121	79.104	79.088	79.071	79.054	79.038	79.021
730	79.004	78.988	78.971	78.955	78.938	78.921	78.905	78.889	78.872	78.856
740	78.839	78.823	78.806	78.790	78.774	78.757	78.741	78.725	78.708	78.692
750	78.676	78.660	78.643	78.627	78.611	78.595	78.579	78.563	78.547	78.530
760	78.514	78.498	78.482	78.467	78.451	78.435	78.419	78.403	78.387	78.371
770	78.355	78.339	78.323	78.308	78.292	78.276	78.260	78.244	78.229	78.213
780	78.197	78.182	78.166	78.150	78.135	78.119	78.104	78.088	78.072	78.057
790	78.041	78.026	78.010	77.995	77.979	77.964	77.949	77.933	77.918	77.902
800	77.887	77.871	77.856	77.841	77.826	77.811	77.795	77.780	77.765	77.750
810	77.735	77.719	77.704	77.689	77.674	77.659	77.644	77.629	77.614	77.599
820	77.584	77.569	77.554	77.539	77.524	77.509	77.494	77.479	77.464	77.449

TABLE 16.—*Rate of change of vapor pressure with temperature for solid carbon dioxide*

[In bars per ° C.]

°C.	0	1	2	3	4	5	6	7	8	9
−130	0.000478	0.000415	0.000359	0.000310	0.000267	0.000230	0.000197	0.000169	0.000144	0.000122
−120	.001764	.001562	.001380	.001217	.001071	.000941	.000825	.000722	.000631	.000550
−110	.005444	.004898	.004400	.003948	.003536	.003162	.002822	.002516	.002239	.001990
−100	.01453	.01325	.01206	.01097	.00997	.00904	.00819	.00741	.00670	.00604
−90	.03450	.03179	.02926	.02691	.02472	.02269	.02080	.01905	.01742	.01592
−80	.07461	.06931	.06435	.05970	.05534	.05126	.04744	.04386	.04053	.03741
−70	.1500	.1403	.1311	.1224	.1143	.1066	.0994	.0926	.0862	.0802
−60	.2861	.2687	.2523	.2367	.2221	.2083	.1953	.1830	.1713	.1604
−50								.3446	.3240	.3045

$pd/d\theta$ at triple point (−56.602° C.)=0.3533 bars per ° C.

TABLE 17.—*Rate of change of vapor pressure with temperature for liquid carbon dioxide*

[In bars per ° C.]

° C.	0	1	2	3	4	5	6	7	8	9
−50	0.2775	0.2692	0.2610	0.2530	0.2452	0.2375	0.2300	0.2226	[1] 0.2154	[1] 0.2083
−40	.3698	.3598	.3500	.3404	.3309	.3216	.3124	.3034	.2946	.2860
−30	.4793	.4676	.4560	.4446	.4334	.4224	.4115	.4008	.3903	.3800
−20	.6070	.5934	.5800	.5667	.5537	.5408	.5282	.5157	.5034	.4913
−10	.7538	.7382	.7228	.7077	.6927	.6779	.6633	.6490	.6348	.6208
−0	.9218	.9039	.8863	.8690	.8518	.8350	.8183	.8019	.7856	.7696
0	.9218	.9399	.9582	.9768	.9957	1.0148	1.0343	1.0540	1.0741	1.0944
10	1.115	1.136	1.158	1.180	1.202	1.224	1.247	1.271	1.295	1.319
20	1.344	1.370	1.397	1.424	1.451	1.480	1.509	1.540	1.571	1.603
30	1.637	1.672								

[1] Undercooled liquid.

Critical temperature=31.0° C.
$dp/d\vartheta$ at triple point (−56.602° C.)=0.2256 bars per ° C.

WASHINGTON, December 15, 1932.

METHODS FOR DETERMINING THE TOTAL ACIDITY OF SOILS

By I. A. Denison

ABSTRACT

A method utilizing the principle of electrometric titration has been successfully applied to estimation of the total acidity of soils. Titration curves of extracts of a large group of diverse soils showed, with few exceptions, fairly well marked inflections from which the acidity of the soils could be readily estimated. The method, however, could not be applied to organic soils which absorbed much more alkali than was required to neutralize their acidity. Values obtained by two additional methods, namely, that of Hissink and that of Page and Williams agreed well with the results given by the titration method. Their use is suggested in estimating the acidity of soils, the titration curves of which do not show an inflection. The indirect method of Page and Williams, which is based on the principle of base exchange, is shown to be well adapted to measuring the acidity of organic soils.

CONTENTS

		Page
I.	Introduction	413
II.	Review of typical methods for determining the total acidity of soils	414
III.	Influence of several factors on the values obtained for total acidity	418
IV.	Description of methods and soils studied	421
V.	Comparison of values for total acidity by different methods	422
VI.	Summary	425
VII.	Acknowledgment	426

I. INTRODUCTION

The determination of the total acidity or the total quantity of ionizable hydrogen in soils has received much attention in recent years, and numerous methods for making this determination have been suggested. Aside from the obvious use of total acidity to indicate the quantity of lime required by an acid soil to neutralize its acidity, expressions involving total acidity, such as the ratio of hydrogen ions to the total quantity of replaceable ions absorbed by a soil are useful as a means of characterizing and differentiating soils. Recently it has been shown that the total acidity of soils has applications wholly apart from agriculture. Several investigators, including the writer, have shown that acidity is a factor in the corrosion of ferrous metals by soils. In a recent publication [1] a relation is indicated between the total acidity of soils and the rate of pitting of buried specimens of iron and steel.[1] A second industrial application of acidity methods is in the field of ceramics in which correlations have been obtained between the physical properties of certain clays and their base exchange capacities.[2] This latter quantity corresponds to the total acidity of a clay in which all replaceable bases have been substituted by hydrogen ions.

[1] Denison, I. A., Methods for Estimating the Corrosiveness of Acid Soils Toward Iron and Steel. Oil and Gas J., vol. 31, No. 19, pp. 83–87. Sept., 1932.
[1] Unpublished data, Bureau of Standards.

II. REVIEW OF TYPICAL METHODS FOR DETERMINING THE TOTAL ACIDITY OF SOILS

Although a large number of methods have been suggested for determining the total acidity of soils, none of these methods has been generally accepted as being entirely satisfactory. The inherent difficulty in making accurate determinations of the total acidity of soils lies in the fact that the reactive materials are colloidal in nature. Since the reactions take place only on surfaces and in somewhat indefinite proportions, it is difficult to follow the course of a reaction, such as neutralization. Neutralization of the difficultly soluble acids of the soil instead of occurring instantaneously, as is the case in ordinary titrations, is apparently complete only after considerable time. Furthermore, because of effects other than neutralization, the inflections in titration curves, which are characteristic of acid-base neutralization in solutions, are usually indefinite when obtained at all, in the usual titration of soil suspensions.

Some idea of the failure of acidity methods to give concordant results when applied to soils may be obtained from the recent work of Crowther and Basu.[3] In comparing the results given by nine different methods applied to eight soils, these investigators expressed the average results obtained from each method as the ratio of unsaturation [4] to that given by a certain method taken as the standard. These ratios were found to vary from 0.55 to 1.02, indicating a wide range of variation in the values obtained for acidity.

This lack of agreement in the values for acidity is due primarily to the fact that the end point of neutralization according to several methods is taken arbitrarily as "neutrality" (pH 7). In fact, Chapman and Kelley [5] state that the content of replaceable H ions as used by them refers to the quantity of barium hydroxide required to bring the reaction of a soil to pH 7. Although this practice is probably justified from certain practical points of view, such as the economical application of lime to soils to neutralize their acidity, it is doubtful that the total acidity of soils can be measured by such procedure. Since the compounds formed by the neutralization of soil acids are probably salts of very weak acids, they would be expected to undergo varying degrees of hydrolysis. As a consequence, the pH value of a soil neutralized by a strong base must be above 7, the exact pH at which the equivalence point occurs depending on the degree to which the salt formed by neutralization is hydrolyzed. Since the acidic material is subject to considerable variation in different soils, it would seem to follow that the equivalence point must likewise be subject to variation. From this point of view titration of soils to any arbitrary pH value would seem to be subject to serious error as a measure of the total acidity.

Although it is desirable in titrating soils to take the inflection in the titration curve as the end point of neutralization, this procedure can not be readily followed in practice, at least by the procedure ordinarily employed. The usual type of titration curve of soils shows

[3] Crowther, E. M., and Basu, J. K., Studies on Soil Reaction VIII, J. Agri. Sci., vol. 21, pp. 689–715, 1931.

[4] The term "unsaturation" applied to the quantity of bases absorbed by soils refers to the quantity of ionizable hydrogen in a soil expressed as percentage of the total capacity of the soil to absorb exchangeable bases. A soil containing no absorbed bases other than hydrogen is 100 per cent unsaturated.

[5] Chapman, H. D., and Kelley, W. P., The Determination of the Replaceable Bases and the Exchange Capacity of Soils, Soil Sci., vol. 30, pp. 391–405, 1930.

a constant curvature near the equivalence point, and in the absence of an inflection the end point can not, of course, be determined.

The failure of titration curves of soils to show an inflection may be considered as being due, at least in part, to the fact that soils, especially those showing marked colloidal characteristics, are capable of absorbing large quantities of alkali in excess of that required for neutralization. In fact, it has been pointed out [6] that certain neutral or slightly alkaline soils may absorb much larger quantities of base than certain acid soils. In spite of this difficulty fairly pronounced inflections have been obtained by Bradfield [7] and by Baver and Scarseth [8] in titrating the colloidal material isolated from soils.

The failure of potentiometric methods to indicate definite end points in titrating soils led to the development of the Hissink method.[9] According to this method increasing quantities of 0.1 *N* $Ba(OH)_2$ are added to definite weights of soil contained in a series of test tubes. Distilled water is then added to each tube to produce a total volume of 50 ml, the tubes are shaken occasionally over a period of three days, and allowed to stand over night. Aliquots of the clear extracts which are alkaline to phenolphthalein are then titrated with standard acid, and the results obtained plotted as ordinates against the quantities of base added as abscissas, all quantities being expressed in milliequivalents. After a few initial values a straight line is obtained. This line is then extended to the base line and the point of intersection taken as the acidity of the soil. Values given by this method are, of course, generally higher than those obtained by titrating to pH 7.

The fact that bases absorbed by soils may be replaced by another base present in large excess has led to the development of methods for determining total acidity based on extraction of the soil with a salt solution and titration of the replaced hydrogen in the extract. Owing to the marked buffering effect shown by salts of weak acids, salts, such as barium and ammonium acetates, which have been adjusted to neutrality, replace a much larger fraction of the total hydrogen than neutral salts, such as the corresponding chlorides. These methods measure the more reactive or more readily replaced hydrogen in the soils, but probably do not usually measure the total hydrogen. Methods employing extraction procedure with subsequent titration of the extract have been employed by Parker,[10] Schollenberger, and Dreibelbis [11] and others.

In addition to methods for determining total acidity by titrating either the soil suspended in water or a salt extract of the soil, indirect methods have been employed which do not involve titration. These methods depend on the fact that the quantity of ionizable hydrogen in a soil is equal to the difference between the total quantity of replaceable bases which the soil can absorb, expressed as equivalents, and the quantity of bases actually present. In other words, the quantity of ionizable hydrogen might be regarded as representing a

[6] Kelley, W. P., and Brown, S. M., Replaceable Bases in Soils, Calif. Agr. Exp. Sta. Tech. Paper 15, 1924.
[7] Bradfield, R., The Saturation Capacity of Colloidal Clay Soils, Proc. First Internat. Cong. Soil Sci., vol. 4, pp. 858–868, 1927.
[8] Baver, L. D., and Scarseth, G. D., The Nature of Soil Acidity as Affected by the SiO_2-sesquioxide ratio, Soil Sci., vol. 31, pp. 159–173, 1931.
[9] Hissink, D. J., Base exchange in soils, Trans. Faraday Soc. vol 20, pp. 551–556, 1925.
[10] Parker, F. W., Methods for the Determination of the Amount and Acidity of Exchangeable Hydrogen in Soils, Proc. First Internat. Cong. Soil Sci., vol. 2, pp. 164–173, 1927.
[11] Schollenberger, C. J., and Dreibelbis, F. R., Analytical Methods in Base Exchange Investigations on Soils, Soil Sci., vol. 30, pp. 161–173, 1930.

156547—33——9

deficit in the total quantity of absorbed alkali and alkaline earth bases. This relation is customarily expressed by the following equation:

$$V = 100\,\frac{T-S}{T}$$

where

V = degree of unsaturation of the soil with respect to replaceable bases.

T = absorption capacity for exchangeable bases in milligram-equivalents.

S = total content of absorbed bases present in soil in milligram-equivelent.

$T-S$ = absorbed hydrogen.

This principle is employed in the method of Page and Williams.[12] In determining the value, T, according to this method the soil is first treated with an excess of calcium carbonate in the presence of 1 N NaCl. After standing for several days, the mixture is extracted with several liters of the salt solution. The hydrogen ions replaced by the sodium ions react with calcium carbonate and an equivalent amount of calcium ions pass into solution. In addition to this quantity of calcium ions, there appears in solution an additional quantity representing the calcium ions originally held by the soil in an absorbed condition. The total quantity of calcium in solution is then determined. The value, S, with respect to calcium, is determined by leaching a second portion of soil with sodium chloride solution, and determining the quantity of calcium in the extract as before. The difference between the values for T and S expressed in equivalents is taken as the total replaceable hydrogen in the soil.

It will be noted that, in determining the values T and S by the method just described, other absorbed bases present in soils are neglected. In practically all soils, except alkali soils, the calcium ion predominates over all others to such an extent that the values for T and S are only slightly lower than would be the case if the other bases were included. However, since it is the difference, $T-S$, which is of importance rather than the actual values of T and S, neglect of the other bases is not a source of error in this method. The Page-Williams method has been studied in considerable detail by Turner.[13] [14]

It should be noted in connection with the "difference" method which has just been described that although the capacity of many soils to absorb alkali seems practically unlimited, the capacity of these soils to absorb bases which are stoichiometrically replaceable by the base of a neutral salt solution is a definite and constant quantity. It is because of this fact that it is possible to distinguish between the quantity of base required to neutralize the acidity of a soil and the total quantity of base which a soil might absorb from an alkaline solution.

From the foregoing discussion of methods for determining the total acidity of soils, it has been seen that several of the methods, at least, do not appear to measure the total acidity of the soil but only some

[12] Page, H. J., and Williams, W., Studies on base exchange in Rothamsted soils, Trans. Faraday Soc., vol. 20, pp. 573–585, 1925.

[13] Turner, P. E., An Investigation of the Method of Page and Williams for the Determination of the Saturation Capacity of Soils, J. Agr. Sci., vol. 18, p. 257, 1928.

[14] Turner, P. E., The State of Unsaturation of the Soil in its Relation to its Field Behavior and Lime Requirement, Soil Sci., vol. 30, pp. 349–381, 1930.

fractional part of it, the values obtained by any one method being determined largely by the pH value selected as the end point of the titration. It has been seen that titration of soil suspensions to the equivalence point is rendered especially difficult by the fact that titration curves of soils do not ordinarily exhibit well-marked points of inflection. Although pronounced inflections should, perhaps, not be expected in view of the strong tendency of soils to absorb alkali, thus obscuring the break in the curve, nevertheless it would seem possible to accentuate the inflection by certain modifications in the titration procedure.

Certain factors which tend to affect the inflection in the titration curve of a soil may be listed as follows: (1) Time of contact between soil and base necessary to establish equilibrium, (2) nature of the base selected for titration, and (3) use of neutral salt solutions. It has been recognized that although the greater part of the neutralization of a soil takes place very quickly, there is a slower reaction which usually continues for some time before equilibrium is established. Slowness in attaining equilibrium is probably due in part to the fact that alkali reaches the inner surfaces of colloidal aggregates only by the slow process of diffusion. Clark and Collins,[15] after an extensive study of equilibrium between soil and electrolyte, conclude that in titrating to pH 7 with continuous shaking, 90 hours is normally required for equilibrium to be attained. Hardy and Lewis,[16] on the other hand, state that little advantage is to be gained in titrating to pH 7 if the time of continuous shaking is lengthened beyond three minutes after each increment of alkali is added.

Although values for the total acidity of soils would be expected to be identical regardless of the alkali used, it has been found that the alkaline earth hydroxides tend to give significantly higher values than the alkali hydroxides when titration is made to pH 7. Thus Hissink and van der Spek [17] found that titration curves of humus soils titrated with calcium hydroxide and sodium hydroxide had different shapes and that considerably more calcium than sodium hydroxide was required to raise the pH of the soils to 7.

The use of a neutral salt solution in determining the total acidity of soils appears to possess some advantage over the use of alkali alone. The high concentration of basic ions in a normal salt solution would be expected to facilitate the attainment of equilibrium between soil and alkali by replacing hydrogen ions from the colloidal complex. Crowther and Martin [18] observed that much higher values were obtained in titrating in the presence of a neutral salt than with alkali alone. The use of salt solution would also have the further effect of flocculating suspended colloidal material, thereby making possible titration of the soil extract by the colorimetric method.

The object of the present study was primarily to ascertain to what extent an inflection in the titration curve could be depended upon to indicate the end point in the titration of soils. Since it did not appear likely that the titration curves of a large number of

[15] Clark, N. A., and Collins, E. R., Equilibrium Between Soil and Electrolytes, and its Influence Upon Some Lime Requirement Methods, Soil Sci., vol. 29, pp. 417–428, 1930.
[16] Hardy, F., and Lewis, A. H., A Rapid Electrometric Method for Measuring Lime Requirements of Soils, J. Agr. Sci., vol. 19, pp. 18–25, 1929.
[17] Hissink, D. J., and van der Spek, J., Über Titrationskurven von Humusböden, Trans. 2d Comm. Internat. Soc. Soil Sci. (Groningen), V. A. pp. 72–93, 1926.
[18] Crowther, E. M., and Martin, W. S., Studies on Soil Reaction VI, J. Agr. Sci., vol. 15, pp. 237–255, 1925.

diverse soils would all show satisfactory inflections, it seemed especially desirable to ascertain whether other methods might not give satisfactory results for the acidity of those soils which did not show definite inflections. If it could be shown that values for the acidity of most soils could be determined equally well by several methods, it would be possible to substitute an alternative method in those cases where the method of direct titration could not be applied.

III. INFLUENCE OF SEVERAL FACTORS ON THE VALUES OBTAINED FOR TOTAL ACIDITY

Before attempting to determine the acidity of soils by the titration method, it was considered important to study the influence of the factors which have been discussed; namely, (1) time necessary to establish equilibrium between soil and alkali, (2) kind of alkali used in titration, and (3) influence of salt solution.

Estimation of the total acidity of soils was made by the method of colorimetric titration, since clear extracts would usually be produced in the normal course of the procedure to be followed. Suspensions which persisted in remaining turbid were clarified by dialysis through a collodion membrane according to the method of Pierre and Parker.[19]

The indicators used were those selected by Clark and Lubs[20] supplemented by phthalein blue, phthalein red, and tolyl red in the higher pH range. The pH of the indicator was adjusted, according to the isohydric principle of Fawcett and Acree,[21] at the acid, midpoint, and alkaline parts of its range. The difference in pH between indicator and test solution was seldom more than 0.2 pH unit.

Ten gram samples of soil ground to pass a 1 mm sieve were placed in a series of Pyrex test tubes. Increasing amounts of 0.045 *N* $Ca(OH)_2$ or 0.05 *N* NaOH were then added in increments one milliequivalent of alkali per 100 g of soil, and the volume brought to 50 ml with distilled water. In testing the influence of salt on the titration values, solutions of NaOH and $Ca(OH)_2$ in 1 *N* NaCl were used, a sufficient volume of 1 *N* NaCl being added to bring the total volume in each tube to 50 ml. The tubes were then stoppered and shaken vigorously three times daily for periods of one and three days. The pH values of the extracts were then plotted against the amounts of alkali added. The neutralization point was then indicated by the inflection in the curve. Especial care was taken at all times to avoid exposing the extracts to carbon dioxide in the atmosphere.

It was usually unnecessary to construct complete titration curves, since only that part of the curve near the equivalence point is actually required. It was desirable, therefore, to form some idea of the approximate acidity of the soil before determination of the exact value was undertaken. The total acidity was roughly estimated by adding to 2 g samples of soil contained in test tubes, standard alkali equivalent to 5, 10, 15, and 20 milliequivalents per 100 g of soil. A few drop of phenolpthalein were then added, the tubes shaken

[19] Pierre, W. H., and Parker, F. W., The Use of Collodion Sacks in Soil Investigations. Proc. First Internat. Cong. Soil Sci., vol. 2, pp. 396–406, 1927.

[20] Clark, W. M., The Determination of Hydrogen Ions. The Williams & Wilkins Co., Baltimore, Md., 1928.

[21] Fawcett, E. H., and Acree, S. F., The Problem of Dilution in Colorimetric H-Ion Measurements. 1. Isohydric Indicator Methods for Accurate Determination of pH in Very Dilute Solutions. J. Bacteriology, vol. 17, pp. 163–204, 1929.

thoroughly, and allowed to stand over night. The first tube in the series which showed a decided pink coloration was taken to indicate the approximate acidity of the soil.

The effects of kind of alkali, of time necessary to reach equilibrium, and the presence of a neutral salt, which were studied using several soils, are illustrated in Figure 1 by titration curves of a sample of Cecil clay. In studying the effect of these factors, sodium and calcium hydroxides were employed and the titration made in the presence of both distilled water and normal sodium chloride. The periods allowed for equilibrium to be established were one and three days. For the sake of clarity the curves which did not show significant differences are not shown in the figure. The curve for $Ca(OH)_2$ and distilled

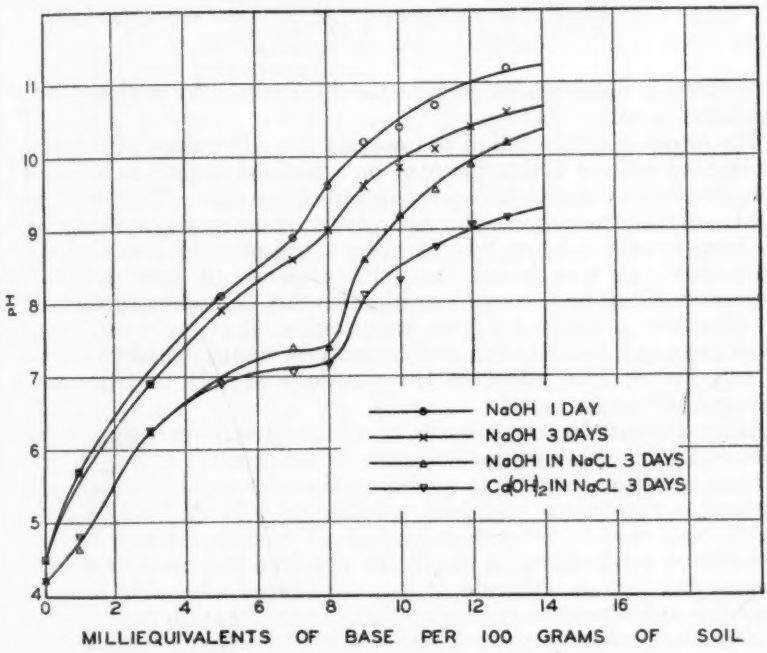


FIGURE 1.—*Influence of several factors on titration of Cecil clay*

water, which is not shown, is similar to that for $Ca(OH)_2 + NaCl$. Similarly, the curves for $Ca(OH)_2$, $Ca(OH)_2 + NaCl$, and $NaOH + NaCl$ were practically the same for the one and three day periods.

As would probably be expected, the nature of the alkali used had no effect on the end point of the titration, although it will be observed that the pH values corresponding to the various concentrations of alkali are very much higher with sodium hydroxide than with the other treatments. It is evident from the table that equilibrium is not obtained with sodium hydroxide in one day. However, equilibrium was established by the other treatments within 24 hours, as previously stated. The presence of the salt solution apparently has no effect on the end point, but it does reduce very markedly the pH values of extracts of the soil containing sodium hydroxide. No such effect was observed in case of extracts containing calcium hydroxide.

Relatively higher pH values of soil suspensions containing sodium hydroxide as compared with the hydroxides of the alkaline earths have also been observed by Hissink and Van der Spek [22] and by Baver [23] in their comparisons of titration curves of various alkali and alkaline earth hydroxides. The high pH values produced by the alkali hydroxides are considered by both Hissink and Baver to indicate that a sodium saturated clay is strongly hydrolyzed in the presence of water. The absorbed sodium ion being more highly hydrated than absorbed ions of the alkaline earths is considered to be more easily dissociated from the clay complex, and hence subject to a greater degree of hydrolysis. This effect may be represented as follows:

$$\left[\begin{array}{c}\text{colloidal}\\ \text{particle}\end{array}\right]\begin{array}{l}Na^+\\ Na^+\\ Na^+\end{array} + HOH \rightleftarrows \left[\begin{array}{c}\text{colloidal}\\ \text{particle}\end{array}\right]\begin{array}{l}H^+\\ Na^+\\ Na^+\end{array} + NaOH$$

This scheme incidentally represents the process by which acidity is produced in soils.

The effect of salt solution in lowering the pH values of the extracts containing sodium hydroxide may be explained in part as a repression of hydrolysis by the high concentration of the salt. This tendency of a salt solution to repress the hydrolysis of an easily hydrolyzed salt has been noted by Jenny [24] in titrating aluminum chloride with sodium hydroxide. It was found that the presence of both sodium and potassium chlorides lowered considerably the pH values of the solution as titration proceeded. The assumption that calcium saturated clays are not subject to marked hydrolysis would explain the absence of any appreciable effect of the presence of salt in titrating with calcium hydroxide.

Although satisfactory results in titrating soils can apparently be obtained with either sodium or calcium hydroxides and with or without salt solution, providing sufficient time for establishment of equilibrium is allowed, a standard solution of 0.05 *N* $Ca(OH)_2$ in 1 *N* NaCl was chosen for determination of acidity. Since one of the alternative methods to be employed required the use of calcium carbonate and sodium chloride, it was considered advisable to maintain a similar anionic and cationic system in the titration procedure. Although the preliminary work did not indicate that a titration period greater than 24 hours was necessary in the case of the soils studied, it was considered desirable in the light of the experience of certain other investigators to allow three days for equilibrium to be established. The use of calcium hydroxide and sodium chloride insured rapid flocculation of the soil particles, thereby making possible titration of the extracts by the colorimetric method.

---

[22] See footnote 17, p. 417.

[23] Baver, L. D., Relation of the Amount and Nature of Exchangeable Cations to the Structure of Colloidal Clay, Soil Sci., vol. 29, pp. 291–308, 1930.

[24] Jenny, H., Behavior of Potassium During the Process of Soil Formation, Res. Bull. 162, Mo. Agr. Exp. Sta., 1931.

IV. DESCRIPTION OF METHODS AND SOILS STUDIED

The methods used in determining the total acidity of the soils selected for study were: (1) Colorimetric titration of the soils by 0.05 *N* $Ca(OH)_2$ in the presence of 1 *N* NaCl, allowing 72 hours contact between alkali and soil. The details of this method have been previously given. (2) The Hissink method modified to include the use of salt solution and by substitution of 0.05 *N* $Ca(OH)_2$ for 0.1 *N* $Ba(OH)_2$. (3) The modified "difference" method of Page and Williams. The principle of this method and an outline of the procedure have been previously given. This latter method would seem to be particularly well adapted to measurement of the acidity of highly absorptive organic soils. Because of the fact that such soils are especially well buffered in the alkaline range it is not likely that a titration curve would show an inflection from which their values for acidity could be determined.

The details of the procedure followed in determining acidity by the "difference" method are as follows. The capacity of the soil to absorb exchangeable bases (T) was first determined. A 25 g sample of soil was placed in a 250 ml Erlenmeyer flask, about 1 g of calcium carbonate added, the soil treated with 150 to 200 ml of 1 *N* NaCl which had been heated to 80° to 90° C., and the mixture maintained near that temperature for one hour with occasional shaking. The mixture was then poured into a 400 ml bottle, shaken over night in an end-over-end shaker and also for 2-hour periods on two succeeding days. After standing over night the extract was decanted and filtered into a 1 liter beaker. A 200 ml portion of salt solution was then added to the soil, the mixture shaken an hour, allowed to settle, and the extract decanted through the filter as before. This process was repeated until 1 liter of extract was obtained. For the final filtration the entire quantity of soil was poured on the filter and washed. The extract was then mixed thoroughly and the calcium present in a 400 ml portion was determined gravimetrically. From the value thus obtained, the quantity of calcium equivalent to the solubility of calcium carbonate in 1 liter of 1 *N* NaCl was subtracted.

The quantity of replaceable calcium present in the soil (*S*) was determined in a manner which was similar to the determination of the exchangeable base capacity, except that no calcium carbonate was added and the shaking was limited to 18 hours. In the case of those soils in which calcium carbonate occurred naturally, a correction was made for the calcium which had been dissolved as carbonate by the salt solution. This quantity was calculated from the amount of bicarbonate in solution, which was estimated by titrating an aliquot portion of the extract with standard acid to the color change of methyl orange.

The quantity of exchangeable hydrogen or the total acidity of the soil (*T*–*S*) was obtained by subtracting from the exchange capacity of the soil the adsorbed calcium found to be present.

The soils selected for study were those in which the test sites of the Bureau of Standards soil-corrosion investigation are located and are described in a previous paper.[25] These soils are diverse in character,

[25] Logan, K. H., Ewing, S. P., and Yeomans, C. D., Bureau of Standards Soil Corrosion Studies 1. Soils, materials and results of early observations Tech. Paper No. 368, 1928.

representing a wide range of texture, parent material, stage of development and geographic distribution. The soils studied, together with their locations are listed in Table 1, in which the values for acidity are shown.

V. COMPARISON OF VALUES FOR TOTAL ACIDITY BY DIFFERENT METHODS

The method of colorimetric titration produced fairly well-marked inflections in the titration curves of the majority of the soils studied. As may be seen from Table 1 definite values for acidity by means of titration curves were obtained in the case of all soils except five. Of

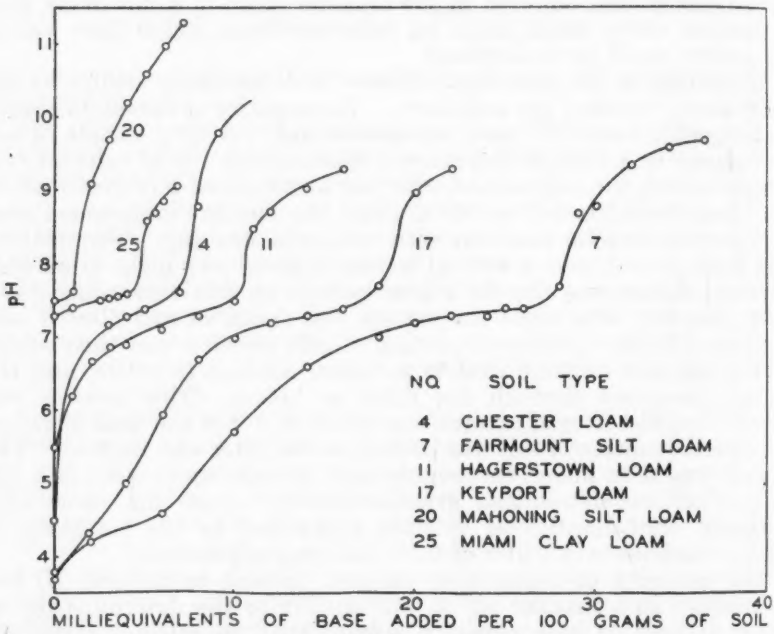


FIGURE 2.—*Titration curves of soils*

this number, three soils, namely, the muck, peat, and tidal marsh, are organic and apparently have an unlimited capacity for absorbing alkali. In the case of several soils it was necessary to estimate the position of the end point by extending the convex and concave portion of the curve and locating the end point on the curve between these extensions. Curves typical of those in which distinct inflections occurred are shown in Figure 2. The results shown in the figure are expressed as milliequivalents of hydrogen per 100 g of air-dry soil. It should be pointed out that the soil designated in Figure 2 and in Table 1 as Fairmount was incorrectly classified, since soils of the Fairmount series are alkaline below the surface horizon.

It is of interest to note in connection with Figure 2, that the values for acidity obtained by titrating to pH 7, as required by some methods,

are approximately one-half as large as those obtained by titrating to an inflection in the curve.

Typical curves obtained by the modified Hissink method are shown in Figure 3. In certain of the curves not shown in the drawing the slopes of straight line connecting the points were much less than those shown in the table. An especially slight slope would seem to indicate market absorption of alkali in excess of that required for neutralization.

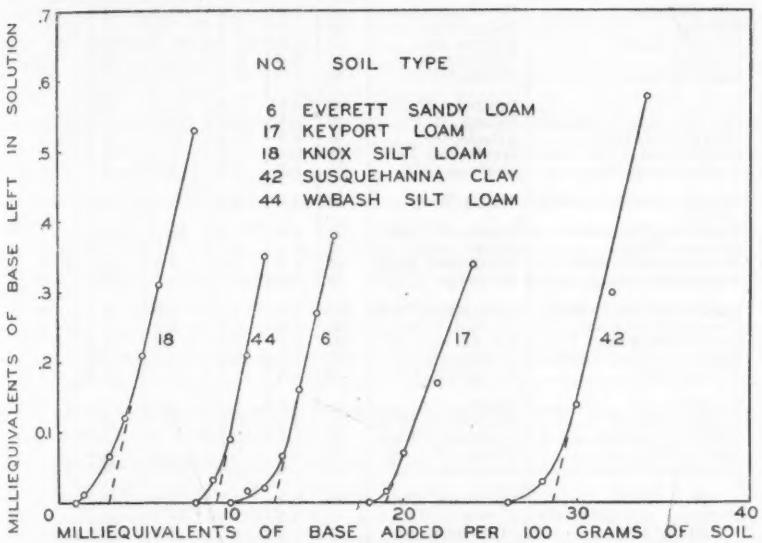


FIGURE 3.—*Titration curves of soils (modified Hissink method)*

The values obtained by the method of colorimetric titration, by the modified Hissink method, and by the modified Page and Williams method are shown in Table 1. The differences between the values obtained by the Hissink and the Page Williams methods as compared with those given by the titration method are also shown in the table. All values are based on the weight of the soil dried in the oven at 105° C.

TABLE 1.—*Comparison of values for total acidity obtained by different methods*

Soil No.	Soil type	Location	Depth	pH of soil [1]	Total acidity			Differences	
					(1) Titration curve	(2) Modified Hissink method	(3) Page-Williams method	Methods 1 and 2	Methods 1 and 3
			Inches		*M. e.*[2]	*M. e.*	*M. e.*	*M. e.*	*M. e.*
1	Allis silt loam	Cleveland, Ohio	90	7.0	11.4	11.2	7.9	−0.2	−3.5
2	Bell clay	Dallas, Tex	40	7.3	3.5	7.5	2.3	+4.0	−1.2
3	Cecil clay loam	Atlanta, Ga	32	5.2	11.5	11.5	10.8	0	−.7
104	Cecil clay	Charlotte, N. C	36	4.6	11.0	10.8	10.7	−.2	−.3
105	Cecil clay loam	Macon, Ga	30	4.8	12.9	12.8	11.7	−.1	−1.2
106	do	Salisbury, N. C	36	4.8	12.8	12.8	10.6	0	−2.2
107	Cecil fine sandy loam	Raleigh, N. C	30	4.8	11.8	12.8	10.4	+1.0	−1.4
108	Cecil gravelly loam	Atlanta, Ga	30	4.9	11.2	11.7	10.7	+.5	−.5
4	Chester loam	Jenkintown, Pa	36	5.6	7.6	7.3	6.9	−.3	−.7
5	Dublin clay adobe	Oakland, Calif	30	7.0	7.5	6.5	6.4	−1.0	−1.1
6	Everett gravelly sandy loam.	Seattle, Wash	36	5.9	12.8	12.8	12.5	0	−.3
7	Fairmount silt loam	Cincinnati, Ohio	40	4.4	31.3	33.0	26.9	+1.7	−4.4
9	Genesee silt loam	Sidney, Ohio	22	6.8	[3]	7.0	.3		
10	Gloucester sandy loam	Middleboro, Mass	30	6.6	3.6	4.8	2.7	+1.2	−.9
11	Hagerstown loam	Baltimore, Md	60	5.3	10.8	11.1	10.5	+.3	−.3
12	Hanford fine sandy loam	Los Angeles, Calif	24	7.1	2.5	2.0	2.3	−.5	−.2
14	Hempstead silt loam	St. Paul, Minn	60	6.2	5.6	5.5	7.2	−.1	+1.6
15	Houston black clay	San Antonio, Tex	36	7.5	5.0	5.0	3.0	0	−2.0
16	Kalmia fine sandy loam	Mobile, Ala	30	4.4	11.8	11.7	14.0	−.1	+2.2
17	Keyport loam	Alexandria, Va	36	4.5	19.1	19.5	19.8	+.4	+.7
18	Knox silt loam	Omaha, Nebr	48	7.3	1.4	3.1	3.1	+1.7	+1.7
19	Lindley silt loam	Des Moines, Iowa	36	4.6	10.9	10.9	10.7	0	−.2
20	Mahoning silt loam	Cleveland, Ohio	50	7.5	1.5	1.8	1.7	+.3	−.2
21	Marshall silt loam	Kansas City, Mo	36	6.2	9.5	9.0	10.4	−.5	+.9
22	Memphis silt loam	Memphis, Tenn	33	4.9	12.8	11.5	9.3	−1.3	−3.5
115	do	Vicksburg, Miss	30	6.9	4.7	5.9	3.6	+1.2	−1.1
24	Merrimac gravelly sandy	Norwood, Mass	33	4.5	12.6	13.1	15.7	+.5	+3.1
25	Miami clay loam	Milwaukee, Wis	36	7.2	4.7	4.8	3.0	+.2	−1.7
26	Miami silt loam	Springfield, Ohio	48	7.3	2.6	3.8	2.7	+1.2	+.1
27	Miller clay	Bunkie, La	30	6.6	3.7	4.8	3.5	+1.1	−.2
29	Muck	New Orleans, La	24	4.2	[4]	[4]	26.8		
30	Muscatine silt loam	Davenport, Iowa	36	7.0	2.6	2.7	1.0	+.1	−1.6
31	Norfolk sand	Jacksonville, Fla	24	4.7	1.8	1.8	2.0	0	+.2
121	do	Tampa, Fla	24	4.8	1.2	1.3	2.6	+.1	+1.4
119	Norfolk sandy loam	Macon, Ga	30	4.7	9.7	10.7	9.7	+1.0	0
120	do	Pensacola, Fla	36	5.7	1.3	1.3	1.4	0	+.1
32	Ontario loam	Rochester, N. Y	48	7.3	.5	2.4	1.1	+1.9	+.6
33	Peat	Milwaukee, Wis	24	6.8	[4]	[4]	33.0		
34	Penn silt loam	Norristown, Pa	34	6.7	7.0	7.1	4.4	+.1	−2.6
35	Ramona loam	Los Angeles, Calif	36	7.3	5.7	5.6	2.9	−.1	−2.8
36	Ruston sandy loam	Meridian, Miss	36	4.5	4.6	4.9	7.3	−.3	+2.7
37	St. Johns fine sand	Jacksonville, Fla	30	3.8	[4]	[4]	15.3		
38	Sassafras gravelly sandy loam.	Camden, N. J	30	4.5	1.7	2.1	3.2	+.4	+1.5
39	Sassafras silt loam	Wilmington, Del	36	5.6	6.6	7.9	6.6	+1.3	0
40	Sharkey clay	New Orleans, La	30	6.0	[3]	9.4	9.2		
41	Summit silt loam	Kansas City, Mo	36	5.5	11.0	12.6	11.1	+1.6	+.1
42	Susquehanna clay	Meridian, Miss	30	4.7	28.2	30.3	31.9	+2.1	+3.7
123	do	Shreveport, La	30	4.1	21.9	22.4	[4]	+.5	
124	Susquehanna silt loam	Troup, Tex	36	4.4	28.1	29.2	25.0	+1.1	−3.1
125	Susquehanna fine sandy loam.	Shreveport, La	42	3.9	28.3	28.8	28.3	+.5	0
43	Tidal marsh	Elizabeth, N. J	36	3.1	[4]	[4]	34.8		
44	Wabash silt loam	Omaha, Nebr	30	5.8	8.8	9.5	9.3	+.7	+.5
47	Unidentified silt loam	Salt Lake City, Utah	36	7.6	3.0	2.8	3.7	−.2	+.7
	Averages				9.4	9.8	10.0	0.67	1.30

[1] Determined colorimetrically in 1 : 2 soil-water extract.
[2] Milliequivalents per 100 grams of soil.
[3] No definite inflection in titration curve.
[4] Not determined.

Comparison of the three sets of values shown in the table indicates that the three methods for determining acidity give substantially the same results. The agreement between the values given by the method of colorimetric titration and the modified Hissink method is with two exceptions less than 2 m. e. per 100 g of soil. The large error of 4 m. e. which occurred in the case of the Bell clay is to be ascribed to the high buffering capacity of this soil immediately above its equivalence point. Because of marked absorption of alkali beyond that required for neutralization, the excess of alkali added in titrating this soil could not be detected by titrating with acid until the equivalence point had been passed.

If the values given by the difference method are compared with those obtained from the titration curve, it will be observed that in spite of the obvious dissimilarity in the two methods, the agreement is generally satisfactory. In approximately 80 per cent of the total number of results the agreement is within 2 m. e. per 100 g of soil. The errors in the difference method are apparently unaffected by the quantity of acid in the soil, but analysis of the data suggests that lower values for acidity by the difference method are slightly more numerous in the heavy clay soils. This is to be expected owing to the difficulty of completely removing absorbed ions from such soils.

From the fact that the results obtained by the three methods under study are in substantial agreement, it seems reasonable to conclude that failure to obtain a satisfactory inflection in the titration curve of a soil does not necessitate the selection of some arbitrary pH value as the end point of neutralization. In determining the acidity of those soils whose titration curves show an uncertain inflection or none at all, it would seem preferable to employ an alternative method. The method best adapted to estimate the acidity of organic soils and other soils especially well buffered in the alkaline range is preferably based on the principle of base exchange. The "difference" method which has been described is well adapted to such soils. Regardless of the capacity of soils to absorb bases, the base exchange capacity is a definite and determinable quantity.

VI. SUMMARY

1. Titration of soil extracts to an inflection in the titration curve was found to be a practical means of determining their total acidity. This method, however, could not be successfully applied to organic soils. Titration with sodium and calcium hydroxides in the presence or absence of sodium chloride solution gave the same results in the case of the few soils used in preliminary work. However, with sodium hydroxide it was necessary to allow a period greater than 24 hours for the establishment of equilibrium.

2. The values obtained by titration were in substantial agreement with the results given by two other methods, namely, the modified method of Hissink and the indirect method of Page and Williams. It is suggested that these methods be used as alternative methods in determining the total acidity of soils when a satisfactory inflection in the titration curve can not be obtained. The method of Page and

Williams, which is based on the principle of base exchange, is shown to be well adapted to measuring the acidity of organic soils.

VII. ACKNOWLEDGMENT

The writer is indebted to Robert B. Hobbs for the determinations of acidity made by the several methods.

WASHINGTON, December 12, 1932.